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Sulfate and Particulate Emissions from an Oxidation Catalyst Equipped Engine

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16 ABSTRACT

Particulate and sulfuric acid emissions were studied in the exhaust of a production 1970 Chevrolet 350 CID 2-barrel engine, with and without a pelleted and monolithic oxidation catalyst treating the exhaust. Particulates were collected at various points along a specially-constructed exhaust system. Total mass and the sulfuric acid content of the particulates were measured, as well as the percent conversion of fuel sulfur content into emitted sulfuric acid under variations in the following operating conditions:

a. Cyclic and constant engine speeds
b. Catalyst temperatures
c. Fuel sulfur contents
d. Catalyst exhaust flow rates
e. Secondary air flows
f. Air fuel ratios

It was found that the total mass and sulfuric acid content of the particulates, as well as % conversion of fuel sulfur content depend mostly on engine speed, catalyst temperature, and fuel sulfur content.

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by

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Grant No. R 801476

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ABSTRACT

Particulate and sulfuric acid emissions were studied in the exhaust of a production Chevrolet V-8 engine. Tests were run without a catalyst in the exhaust system and with the engine equipped with a pelleted or a monolithic catalyst. Particles were collected at points along a specially constructed exhaust system. The weight and sulfuric acid content of the particulate matter, and the percent of fuel sulfur emitted as H_2SO_4 were determined under different operating conditions. The effects of the following parameters were studied during the tests: a) engine speed (tests were performed at various constant speeds in the range 55-96 km h^{-1} and under the 7 mode Federal Test Procedure), b) catalyst temperature in the range 573-773 K, c) fuel sulfur content in the range 0.1-0.5%, d) flow rate through the catalyst, e) amount of secondary air, and f) air-fuel ratio. The results showed that the sulfuric acid and particulate emissions and the sulfur conversion depend mostly on the speed, catalyst temperature, and fuel sulfur content. Within the temperature range and secondary air range studied, the type of catalyst, the air-fuel ratio, and the amount of secondary air did not seem to affect the results significantly.

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1. INTRODUCTION

Gasolines contain a small amount of sulfur which, if the engine is not equipped with a catalyst, is emitted mostly in the form of sulfur dioxide. When the engine is equipped with an oxidizing catalyst some of the sulfur dioxide is converted into sulfur trioxide which, combining rapidly with water vapor in the exhaust, is emitted in the form of sulfuric acid. Thus, while oxidation catalysts reduce gaseous emissions they give rise to the emission of sulfuric acid [1-6]. In addition, the installation of oxidation catalysts in automobile exhaust systems causes an increase in the amount of particulate matter emitted [2,3,4,5].

Owing to the possible problems created by the increased sulfuric acid and particulate emissions from catalyst equipped engines, it would be desirable to understand the mechanisms and parameters which control such emissions, and to determine the amounts of sulfuric acid and particulates emitted. In recent years several investigations have been addressed to this problem. Nevertheless many aspects of the problem remain unresolved. Sulfuric acid and particulate emissions from actual engines operating at steady and cyclic speeds were reported in refs. [2-7]. These studies do not indicate fully the important role of the catalyst temperature because this temperature was either not reported [5], or was varied only over a limited range (794-939 K) [2-7]. Sulfate emissions in simulated catalyst-exhaust systems were studied by Nikker et al [8], Hammerle and Nikker [9]. The storage of sulfates in catalysts was investigated by Hammerle and Nikker [9].

Results are not yet available to indicate the full effects of engine variables, fuel sulfur content, and catalyst temperature on the sulfuric acid and particulate emissions from an actual spark ignition engine equipped with

oxidation catalysts. The overall objective of this investigation was, therefore, to study the influence of these parameters on emissions from a Chevrolet V-8 engine operating on a test stand dynamometer. Specifically, the amount of particulate matter and sulfuric acid emitted and the percent of the fuel sulfur emitted as sulfuric acid (sulfur conversion) were measured as a function of a) engine speed (both steady and cyclic), b) fuel sulfur content, c) catalyst temperature, d) flow rate through the catalyst, e) amount of secondary air, and f) air fuel ratio. The tests were performed with both a pelleted and a monolithic oxidation catalyst.

II. EXPERIMENTAL APPARATUS

The apparatus employed in this study was essentially the same as the one used by Sampson and Springer [10] and by Hanley and Springer [11]. Therefore, only a brief summary will be given to indicate the changes made and to facilitate the reading of the report.

The apparatus consisted of the engine, the simulated exhaust system, and the sampling train. These components are described in the following sections.

2.1 Engine and Fuel

The engine used was a 350 CID 250 HP Chevrolet V-8 production engine. The engine specifications are given in Appendix A.

The engine was mounted on a Midwest Dynamatic eddy current dynamometer test stand located in a test cell in the Automotive Engineering Laboratory at The University of Michigan. The engine and dynamometer were instrumented to monitor and control coolant temperature, oil temperature and pressure, manifold vacuum, exhaust pressure, and engine speed and load. The air flow rate to the engine was measured by a rounded approach air cart manufactured by General Motors Corporation. The fuel flow rate was measured with a burette.

Tests were conducted using Indolene HO 0 (clear) fuel. Di-t-butyl disulfide was added to adjust the sulfur content of the fuel to the desired value. The physical and chemical properties of the fuel are given in Appendix B.

The engine was lubricated with Valvoline 10 W 40 oil, which is typical of commercially available motor oils. The oil, oil filter, and PCV valve were changed at 40 hour intervals.

2.2 Simulated Exhaust System

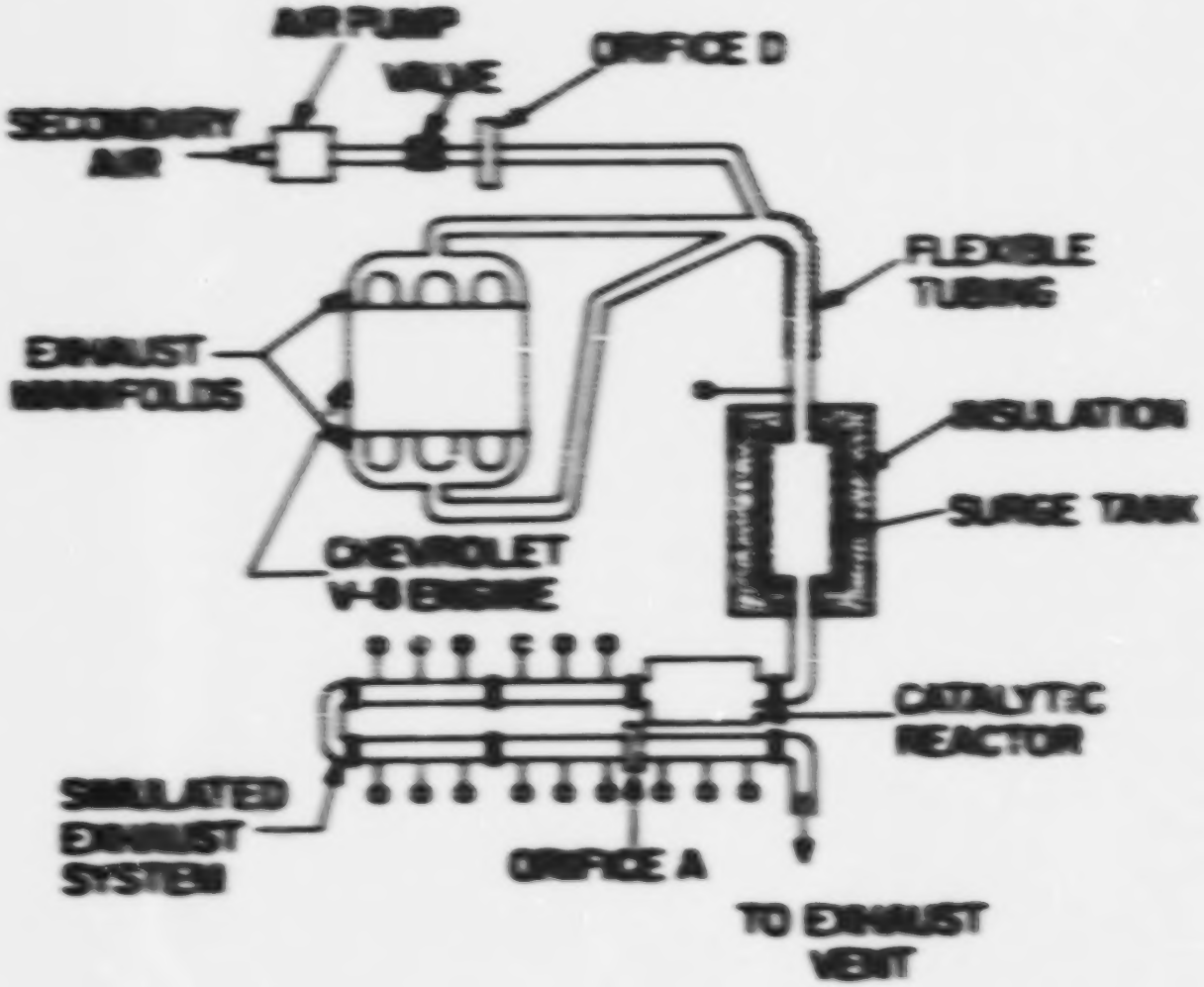
Tests were first conducted under cyclic conditions without the catalysts. Then, in turn a pelleted and a monolithic catalytic reactor were installed in the exhaust system and tests were performed with each catalyst under steady and cyclic operating conditions. In the following paragraphs the basic exhaust system without the reactor is first described. The changes made to install the reactors are outlined subsequently.

The exhaust system, connected to the engine, consisted of the standard exhaust manifolds and cross-over pipe, a surge tank, a 4.27 m long 50.8 mm diameter pipe, and a sharp edged orifice (Fig. 2.1).

The surge tank was a 304 mm diameter 600 mm long steel cylinder, insulated with a wrapping of kaowool. The surge tank was added to reduce the pressure and flow fluctuations in the exhaust (Sampson and Springer [10]).

The simulated exhaust system consisted of three 600 mm long black pipe sections, a 180° bend followed by 4 additional 600 mm sections of black iron pipe. There were six holes in each of the sections. Three 1/8 NPT holes were located along the top and three 1/4 NPT holes along the sides to allow for the installation of thermocouples and sampling probes, respectively. All holes were fitted with plugs when not in use.

A 22.2 mm sharp edged orifice (Orifice A), made to ASME specifications, was placed at the end of the simulated exhaust system. The purpose of this orifice was to measure the exhaust flow rates during cyclic sampling, as described in the next section.


AIR PUMP
VALVE
ORIFICE D
SECONDARY AIR
FLEXIBLE TUBING
EXHAUST MANIFOLDS
INSULATION
SURGE TANK
CHEVROLET V-8 ENGINE
CATALYTIC REACTOR
SIMULATED EXHAUST SYSTEM
ORIFICE A
TO EXHAUST VENT

2.3 Catalysts

Emissions with two catalysts were investigated. One was a pelleted catalyst supplied by General Motors Corporation, the other was a monolithic catalyst supplied by Engelhard Industries (Appendix A).

The catalytic reactors were installed in place of the first segment of the simulated exhaust system. No other modifications of the exhaust system were necessary.

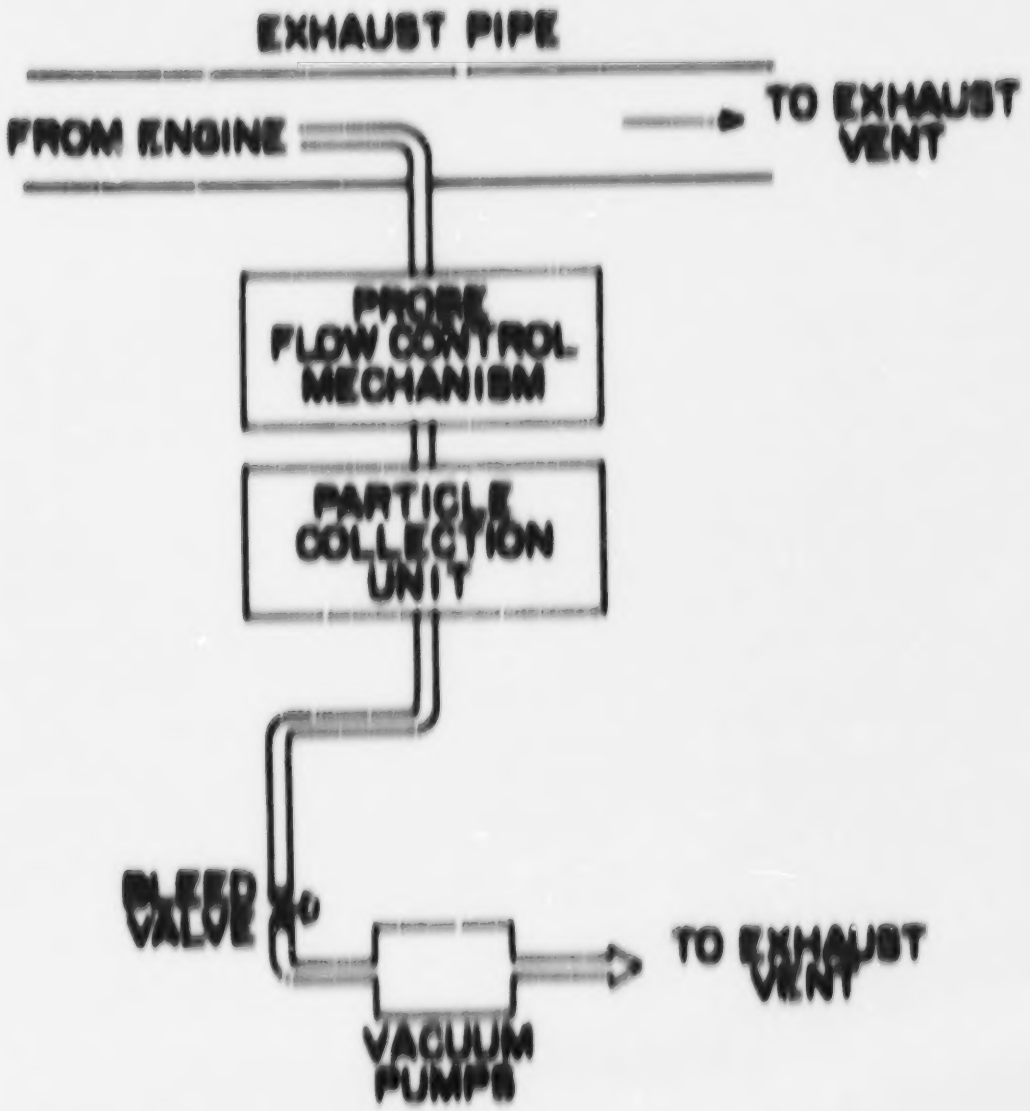
After the tests with the pelleted catalytic reactor were completed the reactor was removed and the monolithic catalytic reactor was installed in its place. The monolithic reactor was designed to process only half the volume of the exhaust gas. Therefore, for the monolithic reactor only four of the eight cylinders (the right bank of cylinders) were connected to the simulated exhaust. The other four cylinders were connected directly to the test cell exhaust vent.

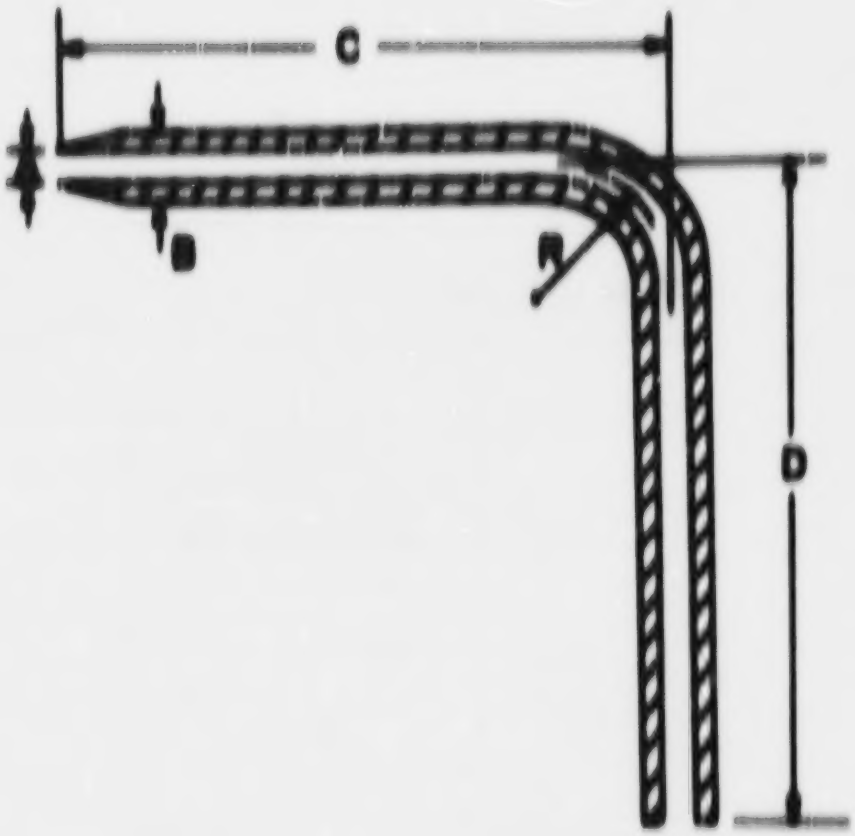
For both catalysts secondary air was injected into the simulated exhaust (before the surge tank) by an air pump driven by a V belt from the crankshaft pulley. The amount of secondary air was controlled by a valve and was measured by an 18 mm sharp edged orifice (Orifice D, Fig. 2.1) made to ASME specifications.

2.4 Sampling Train

The sampling train consisted of a probe, a particle collection unit, a heat exchanger, a flow control mechanism, and two vacuum pumps (Fig. 2.2). Each of these components is described below.

Two different size probes were utilized in the course of this study. They were constructed of 316 stainless steel tubing and had the dimensions given in Fig. 2.3. The larger probes were used when the sample was undiluted.


EXHAUST PIPE
FROM ENGINE
TO EXHAUST VENT
PROBE
FLOW CONTROL MECHANISM
PARTICLE COLLECTION UNIT
BLEED VALVE
TO EXHAUST VENT
VACUUM PUMPS



PROBE	A	B	C	D	R
I	3.98	6.35	114.2	160.3	24.6
II	2.66	4.99	51.5	56.1	11.5

All Dimensions in mm
Material: 316 Stainless Steel

Fig. 3.4 Geometry of probes used in the study.

the smaller ones were used when the sample was diluted with ambient air (during cyclic sampling the larger probes were used in both cases). The probes were located in the center of the exhaust pipe facing the direction of the flow.

The particle collection unit consisted of a single filter (Fig. 3.4). The matter collected on the filter was analyzed to determine particulate and H_2SO_4 emission.

The filters used were Gelman 47 mm diameter type A glass fiber placed in a modified Gelman 2220 filter holder.

The entire collection unit was surrounded with beaded heaters and enclosed in a 25 mm thick wrapping of kaowool held in a sheet metal shell. The current to the heaters was controlled by voltage controllers. The temperature of the gas sample was measured with chromel-alumel thermocouples inserted into the gas stream on both sides of the filter holders.

The exhaust gases could be diluted with ambient air to lower the dew point of the gas mixture and thus avoid condensation of water in the filter. The flow rate of the dilution air was controlled by the mechanism described below.

The flow rate through the probe and the amount of dilution air must be carefully regulated through the tests. The flow rate through the probe must be adjusted to the proper value for isokinetic sampling (Hanley and Springer [11]). The dilution air was kept constant at an 8:1 dilution ratio. At steady operating speeds flow rates of the dilution air and the total sample were measured by wet test meters installed in the system and the flow rates were set appropriately. Under cyclic operating conditions the flow rates through the probe and the dilution system were modified and adjusted

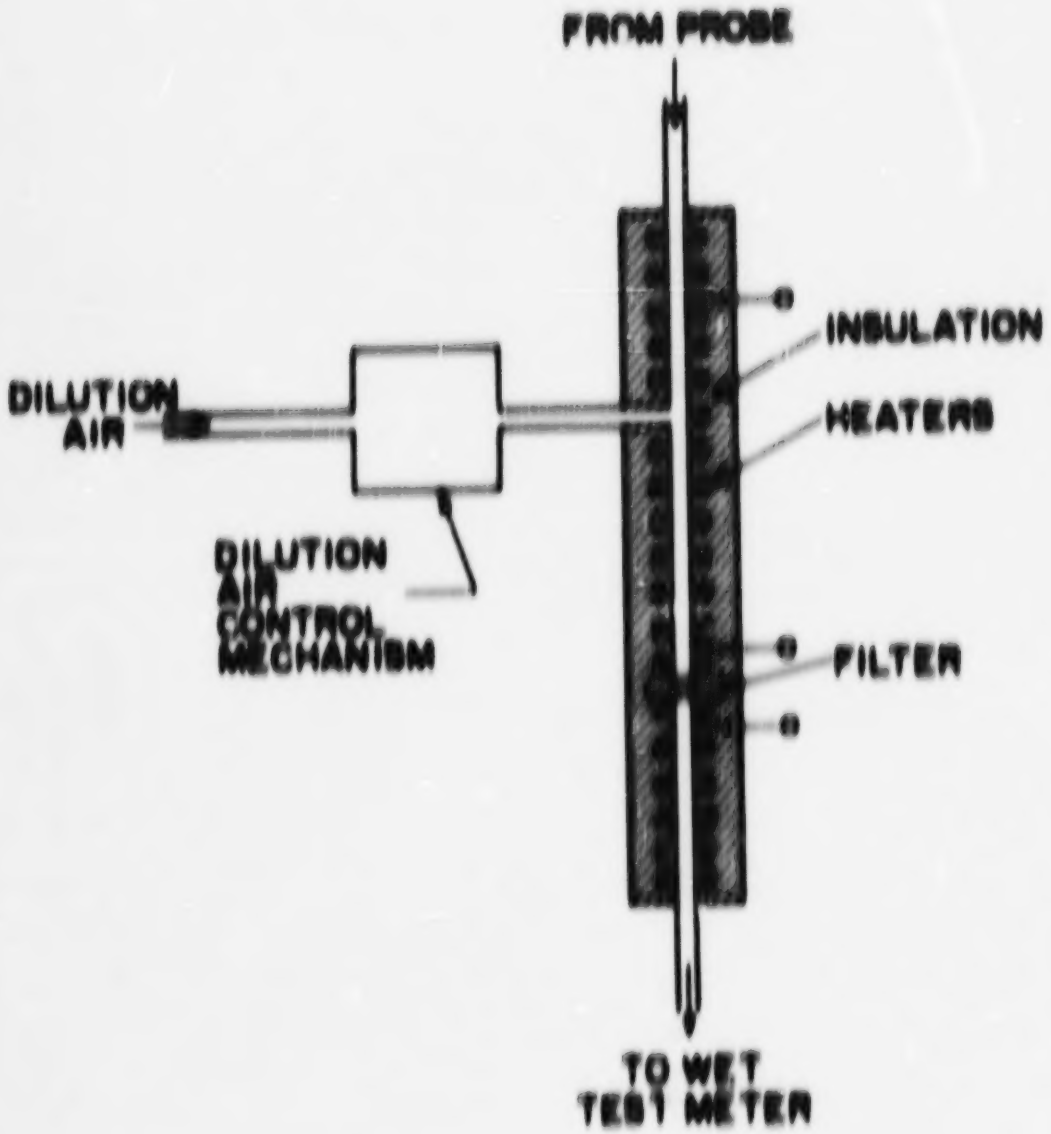
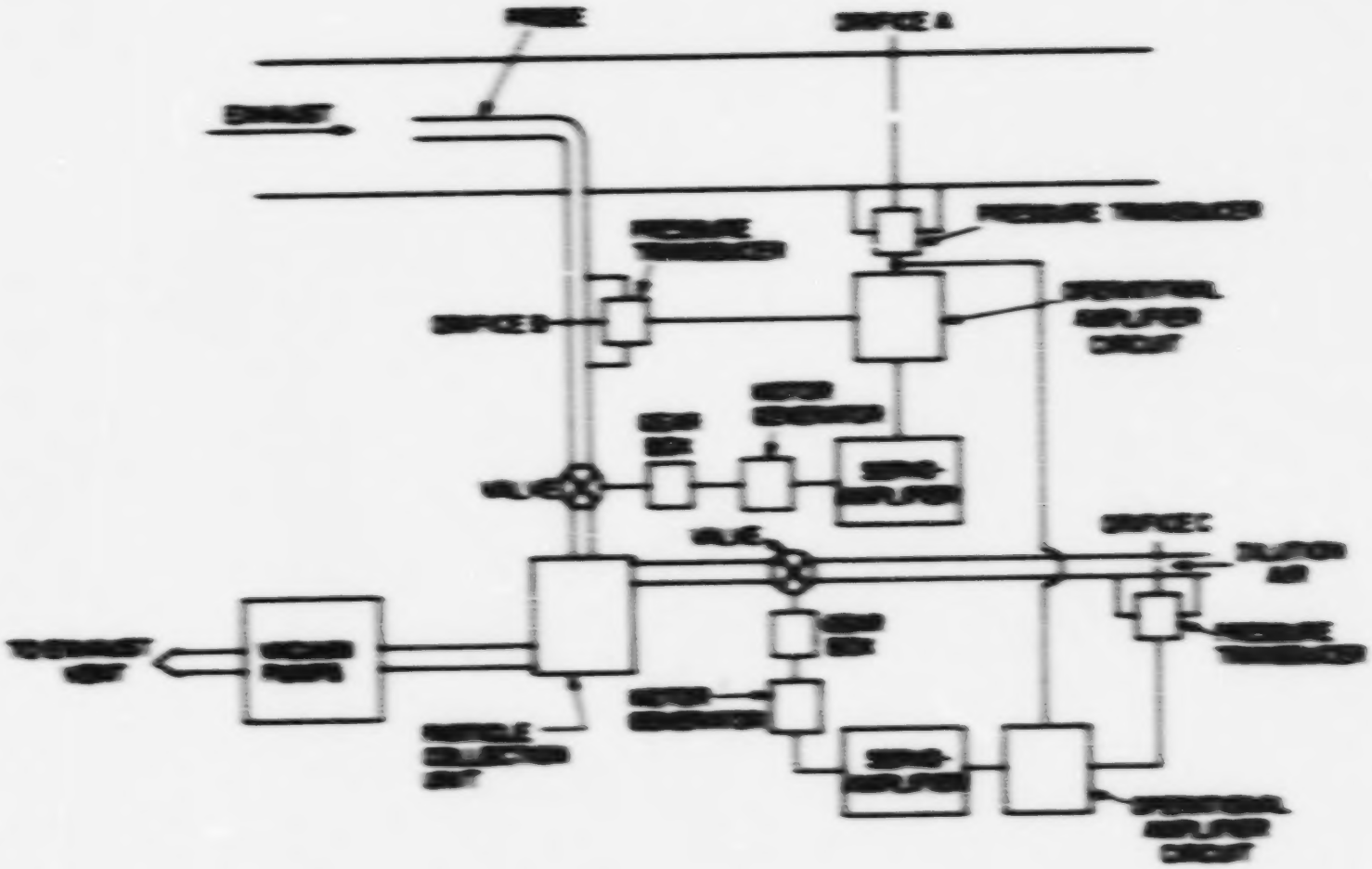


Fig. 2.1. Schematic of the collection unit. Open circles represent thermocouple locations.

continuously. To accomplish this a special flow control system was designed (Fig. 2.5). The flow rate through the probe was regulated as follows. A standard 1.1 mm diameter sharp edged orifice (Orifice B) was installed in the sampling line (Fig. 2.5). The pressure drop across this orifice was measured by a Piran 0 - 0.1 psi differential pressure sensitive transistor immersed in a silicon oil bath to minimize temperature fluctuations. The pressure drop across the orifice in the exhaust system (Orifice A) was measured by a Bahm FT (C) 71 potentiometer type differential pressure transducer. The signals from the two transducers were compared on an Analog Devices 118A Operational Amplifier. A schematic of the amplifier circuit is given in Fig. 2.6. The difference in the two signals was amplified by an ASI/SERVO Systems Model A-170 DC error signal servoamplifier (Fig. 2.6) and fed to a Kollsman 800010A050, 115 volt 2 phase, 2 pole motor generator. This motor generator was connected to a stainless steel Whitey 1RS4 type valve through a 50:1 ratio link "high-precision" gear box. The flow rate through the probe was regulated by the valve.

The amount of dilution air was controlled by a similar control system (Fig. 2.5). The orifice in the dilution air line was 5.6 mm in diameter. The pressure transducer used was a Bourns Model 501 differential pressure transducer and the valve used to control the flow was a Whitey 1RS8 brass valve.

The voltage necessary for the pressure transducers was provided by a Kepco Model CK18-5 and a Thornton 2011 type DC power supply while the servoamplifier and the motor generator were connected to the 117 volt AC line. The orifices were calibrated under steady state conditions. The orifice in the exhaust system (Orifice A) was calibrated with a rounded approach air cart manufactured by General Motors Corporation. The orifices in the sampling line (Orifice B) and in the dilution air line (Orifice C) were calibrated using the wet test meters.



Two high vacuum pumps were used to provide the flow through the sampling train.

III. EXPERIMENTAL PROCEDURE

All tests were performed following the same sequence of steps: a) the engine and exhaust system were conditioned, b) particulate samples were collected, c) the weight of the collected particles was measured, and d) the samples were analysed for sulfate content.

3.1 Test Conditions

A summary of the test conditions under which the samples were taken is given in Table (3.1).

In test series I and II samples were collected at different positions along the simulated exhaust system. In all other tests the samples were collected at one position 400 mm downstream of the catalytic reactor. Tests III through XI were performed first with the pelleted reactor. The tests were then repeated with the monolithic catalytic reactor.

The last column in the table describes the various variables studied during each test.

3.2 Engine and Exhaust Conditioning

Before taking any data the engine and exhaust system were operated at the test conditions to allow the emissions to stabilize.

Prior to the present study the engine had been operating with Indolene HO 0 (clear) fuel. Therefore, before test I the engine was conditioned for six hours only. The results obtained in these tests did not change with time indicating that the six hours conditioning time was sufficient.

When a different catalytic reactor was installed, the system was conditioned the equivalent of 2500 km at 88 km h^{-1} with fuel containing 0.1% sulfur (in addition, the pelleted catalyst had been previously conditioned the equivalent of 8,000 km at 88 km h^{-1} with fuel containing 0.01% sulfur). Before the start of each new series of tests, the engine and the exhaust system were conditioned for three hours.

Table 5.1 Test Conditions

Test Series	Condition	Engine Speed (RPM)	Engine Load (BHP	A/F Ratio	Ignition Spark Advance	Road Speed Equivalent	Test
I	Idle	-	-	-	4°	Static	-
II	Peak Power	3400	24.5	14.6	4°	88 km h^{-1} Cruise	H_2S_0 Concentration
III	Peak Power & Maximum	3400	24.5	15.0	4°	88 km h^{-1} Cruise	Secondary Air and Space Velocity
IV	Peak Power & Maximum	3400	24.5	15.0	4°	88 km h^{-1} Cruise	Fuel Sulfur Content
V	Peak Power & Maximum	3400	24.5	15.0	-6°	88 km h^{-1} Cruise	Spark Retard
VI	Peak Power & Maximum	3400	24.5	17.5	4°	88 km h^{-1} Cruise	A/F Ratio
VII	Peak Power & Maximum	3400	24.5	16.*	4°	88 km h^{-1} Cruise	A/F Ratio
VIII	Peak Power & Maximum	2000	30.0	15.0	4°	96 km h^{-1} Cruise	Secondary Air
IX	Peak Power & Maximum	2000	30.0	15.0	4°	96 km h^{-1} Cruise	Fuel Sulfur Content
X	Peak Power & Maximum	2000	30.0	17.0	4°	96 km h^{-1} Cruise	A/F Ratio
XI	Peak Power & Maximum	2000	30.0	15.0	4°	96 km h^{-1} Cruise	Space Velocity
XII	Peak Power & Maximum	2000	30.*	15.0	4°	96 km h^{-1} Cruise	Secondary Air

Test Series	Conditions	Engine Speed (RPM)	Engine Load BMP	A/F Ratio	Injector Spark Advance	Road Speed Equivalent	Test
[illegible]	[illegible]	1500	11.7	15.0	4°	44 lbs h^{-1} Constant	Fuel Sulfur Content
[illegible]	[illegible]	1500	11.7	15.7	4°	44 lbs h^{-1} Constant	A/F Ratio
[illegible]	[illegible]	1500	11.7	16.5	4°	44 lbs h^{-1} Constant	A/F Ratio
[illegible]	[illegible]	1500	11.7	15.0	4°	44 lbs h^{-1} Constant	Space Velocity
[illegible]	[illegible]	750	5.9	15.0	4°	35 lbs h^{-1} Constant	Recirculation Air
[illegible]	[illegible]	750	5.9	15.0	4°	35 lbs h^{-1} Constant	Fuel Sulfur Content
[illegible]	[illegible]	750	5.9	15.0	4°	35 lbs h^{-1} Constant	Space Velocity
[illegible]	[illegible]	-	-	-	-	FTP	Fuel Sulfur Content

3.3 Test Procedure

A typical test was performed in the following manner. The probe was placed in the location under study, the filters were weighed, placed in the collection unit, and the system was warmed up.

For steady state sampling the engine was run at fast idle for 5 minutes. Then the speed was increased to the operating speed and the torque was increased until the desired load was reached. The engine was then run for about 60 minutes to allow for temperatures and particulate emissions to stabilize. This is particularly important for tests with catalytic reactors because the reactors tend to store H_2SO_4 while cold and release it when they warm up [9]. For cyclic tests the system was warmed up through 10 cycles before sampling.

After the engine warmed up, the temperature of the collection unit was adjusted to the appropriate value and sampling started. When the sampling was not diluted its temperature was adjusted to the same value as that of the exhaust gas at the location of the probe. When the sample was diluted the temperature of the collection unit was kept at a temperature which was lower than the temperature of the exhaust at the location of the probe.

During steady operation (test 1 through 11) the temperatures of the sample and the catalyst were recorded every five minutes. During cyclic operation the temperatures were measured at the end of each cycle. It is noted that the catalyst temperature was measured with a thermocouple inserted into the reactor.

In addition to these temperatures the following parameters were recorded throughout each test: a) temperature and pressure of the gas through the wet test meters, b) the engine speed and load, c) fuel flow rate, d) air flow rate, e) manifold vacuum, f) atmospheric pressure, and g) room temperature.

After each test the filters were placed for 24 hours in an airtight container containing $CaCl_2$ as desiccant. After 24 hours the filters were weighed and prepared for chemical analysis. The weight of the filter indicated the amount of particulates in the exhaust. The chemical analysis provided the sulfate content of the particulate sample.

3.4 Measurement of Sulfuric Acid Content:

The sulfuric acid content of the collected particulate sample was determined by the Barium-Thorin titrimetric procedure [13,14].

The filter was placed in a covered Pyrex flask containing 50 ml of deionized water. After 12 hours, 25 ml of the liquid were taken from the flask, and placed in a centrifuge for 15 minutes to separate out filter fibers. Following the centrifuging 15 ml of the liquid were passed through a cation exchange resin to remove all positive ion interferences. This liquid was then diluted with deionized water to give a total volume of 25 ml. Ten ml of this solution were mixed with 40 ml of isopropanol. Two drops of thorin indicator solution were added to this liquid. The liquid sample thus prepared was titrated with a 0.001 molar solution of $Ba(ClO_4)_2$ diluted in a mixture containing 20% deionized water and 80% isopropanol. The change in color of the liquid was monitored with a Bausch and Lumb Spectronic 20 colorimeter by measuring the change in absorbance of the solution at a wavelength of 520 nm. The amount of titrant added up to the end of the titration was proportional to the H_2SO_4 concentration in the sample.

The titrant solution was calibrated against a solution of H_2SO_4 of "known" concentration. This "known" solution was calibrated by titrating it with a $NaHCO_3$ solution using a glass electrode ph meter to monitor the titration.

IV. RESULTS

The major objective of this investigation was to evaluate the parameters which affect the sulfate and particulate emissions from spark ignition engines equipped either with a monolithic or with a pelleted catalyst. Particular attention was focused on the effects of engine speed, catalyst temperature, fuel sulfur content, air fuel ratio, and amount of secondary air on the amount of particulate matter emitted, on the amount of sulfuric acid emitted, and on the sulfur conversion rate.

It is important to note that in the following tests the effects of the various parameters were separated. This was accomplished by varying one parameter at a time. For example the temperatures of the catalysts were regulated by heating tapes and were thus unaffected by the engine speed or the secondary air. This must be borne in mind when evaluating the data and when comparing them to the results in the previous tests where generally several parameters were varied simultaneously.

4.1 Particulate Emission

In order to establish the proper sampling conditions for the catalyst equipped engine, the particulate emission from the engine was measured both with and without the catalysts. For the engine operating on unleaded fuel and without the catalyst, particulate emission as a function of exhaust temperature is shown in Fig. 4.1 for 55 and 88 km h^{-1} cruise conditions (steady speeds) and for the 7 mode Federal Test Procedure. For exhaust gas temperatures above 500 K the particulate emission remains constant. Particulates collected above this temperature are mostly carbon formed in the combustion chamber due to the dehydrogenation of hydrocarbons [10,11,14]. Below 500 K there is a large increase in particulate emission due mostly to condensation of high molecular weight organic compounds present in the exhaust gas [15-18].

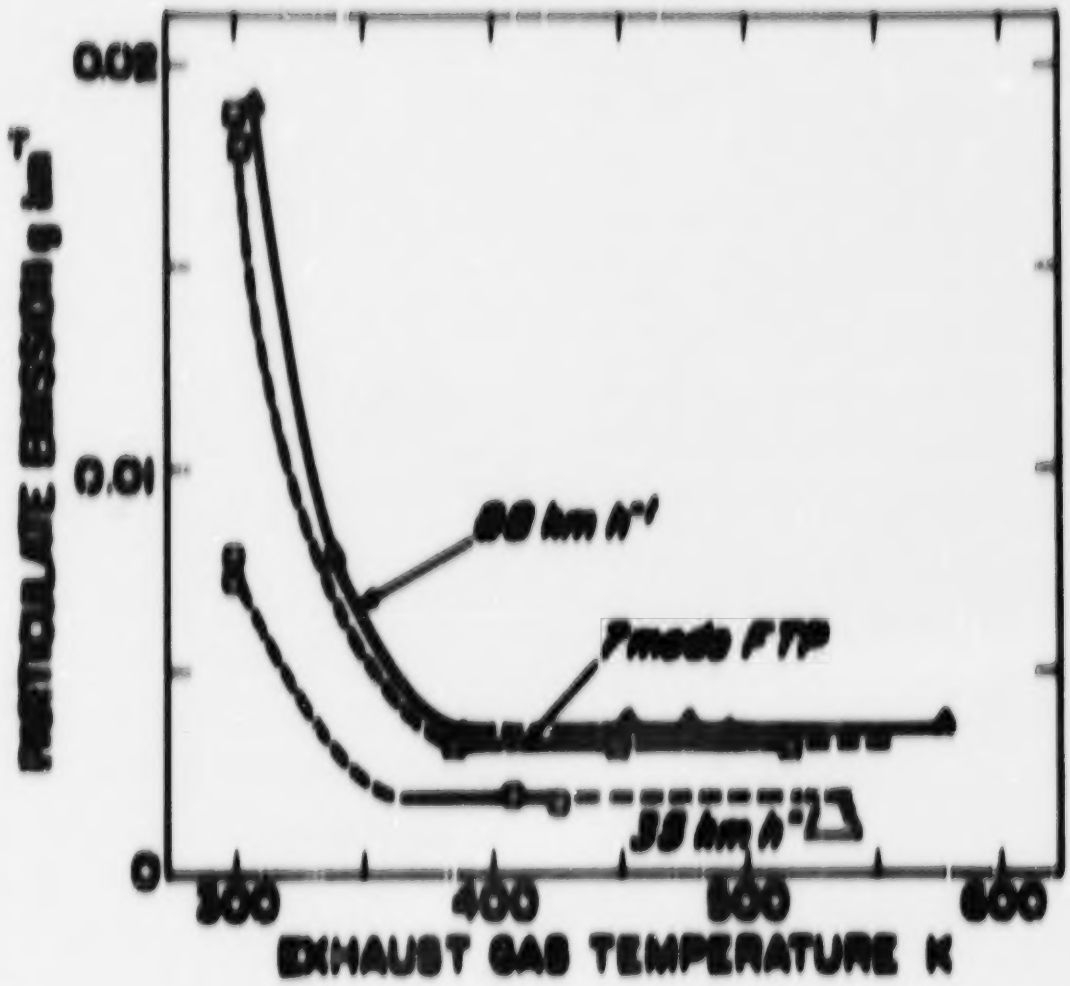


Fig. 4.1. Particulate emission versus exhaust gas temperature during 7 mode federal test procedure, and 55 km h⁻¹ and 80 km h⁻¹ cruise conditions. Indolene HO 6 fuel (——) 1 Hz to data.

It is noted that during the 7 mode Federal Test Procedure approximately twice the amount (by weight) of particulates is emitted as at 55 km h^{-1} steady speed (55 km h^{-1} corresponds to the average speed of the cycle). A similar trend was observed by Ter Haar et al [19].

Particulate emission as a function of exhaust gas temperature was also measured with fuel containing 0.01% sulfur (Fig. 4.4). These tests were performed both with and without the catalyst with the objective of determining the exhaust gas temperature at which most of the sulfuric acid condensed. Above ≈ 390 K the results with and without the catalyst agree closely, suggesting that most particles collected are carbon directly emitted from the combustion chamber [10,11,14]. Deposition in the catalyst may account for the small difference in the results. There is a sharp increase in the amount of particulate matter emitted below 390 K. In the absence of the catalyst this increase is due to condensation of heavy hydrocarbons [15-18]. For the catalyst equipped engine the increase is most likely due to condensation of sulfuric acid. Below 350 K the amount of particulate matter emitted remained constant when using a catalyst, indicating that most of the sulfuric acid condensed out of the gas stream. Therefore, in all subsequent tests the collection unit was kept in the 305-315 K temperature range by diluting the sample with ambient air (dilution ratio 8:1). These temperatures are appropriate also when fuels with higher sulfur content (i.e. sulfur content higher than 0.01%) are used since in this case the condensation process is completed at even higher temperatures.

For steady engine speeds the effects of speed, fuel sulfur content and catalyst temperature on the amount of particulate matter emitted are shown in Fig. 4.5. The lines shown in this figure were calculated by the following expression

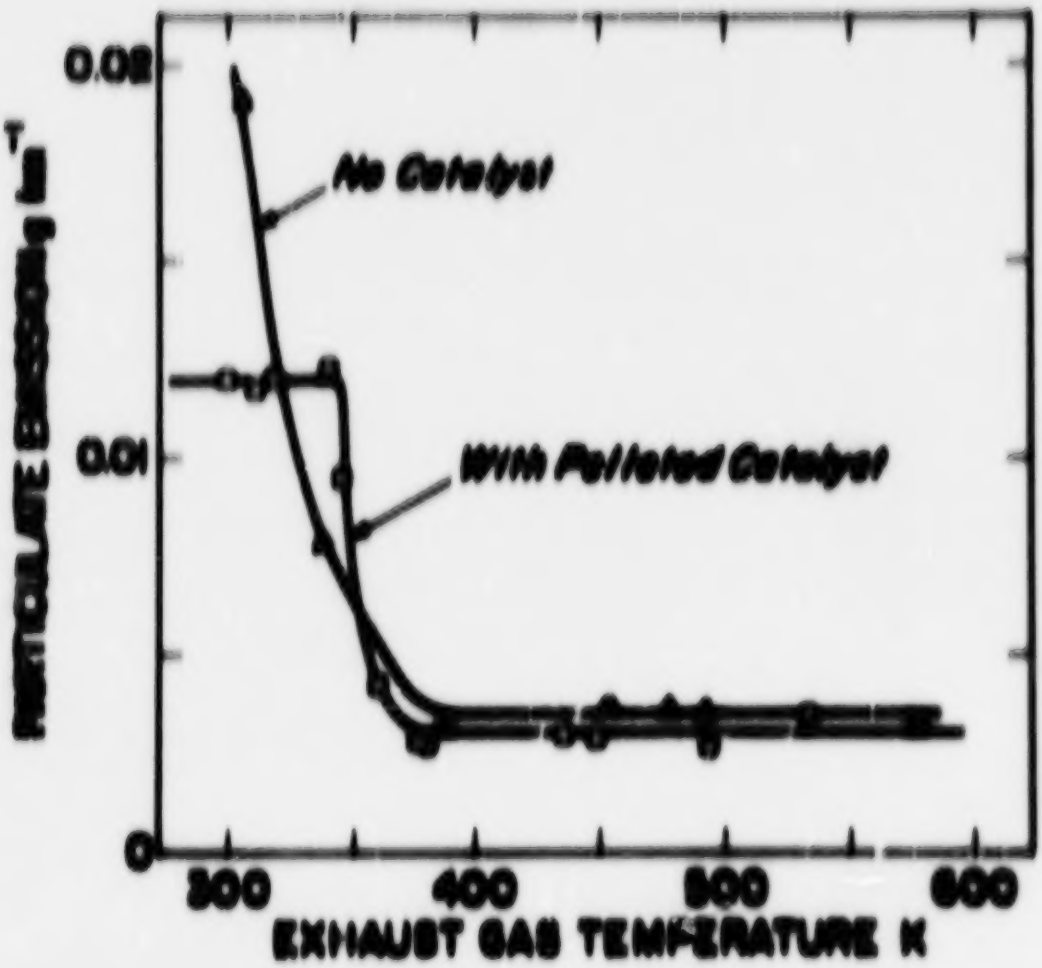


Fig. 4.2. Particulate emission with and without a pelleted catalyst. 88 km h⁻¹ cruise condition. Catalyst temperature 750K Indolene (B) 1 fuel with 0.01% sulfur content. (——) fit to data.

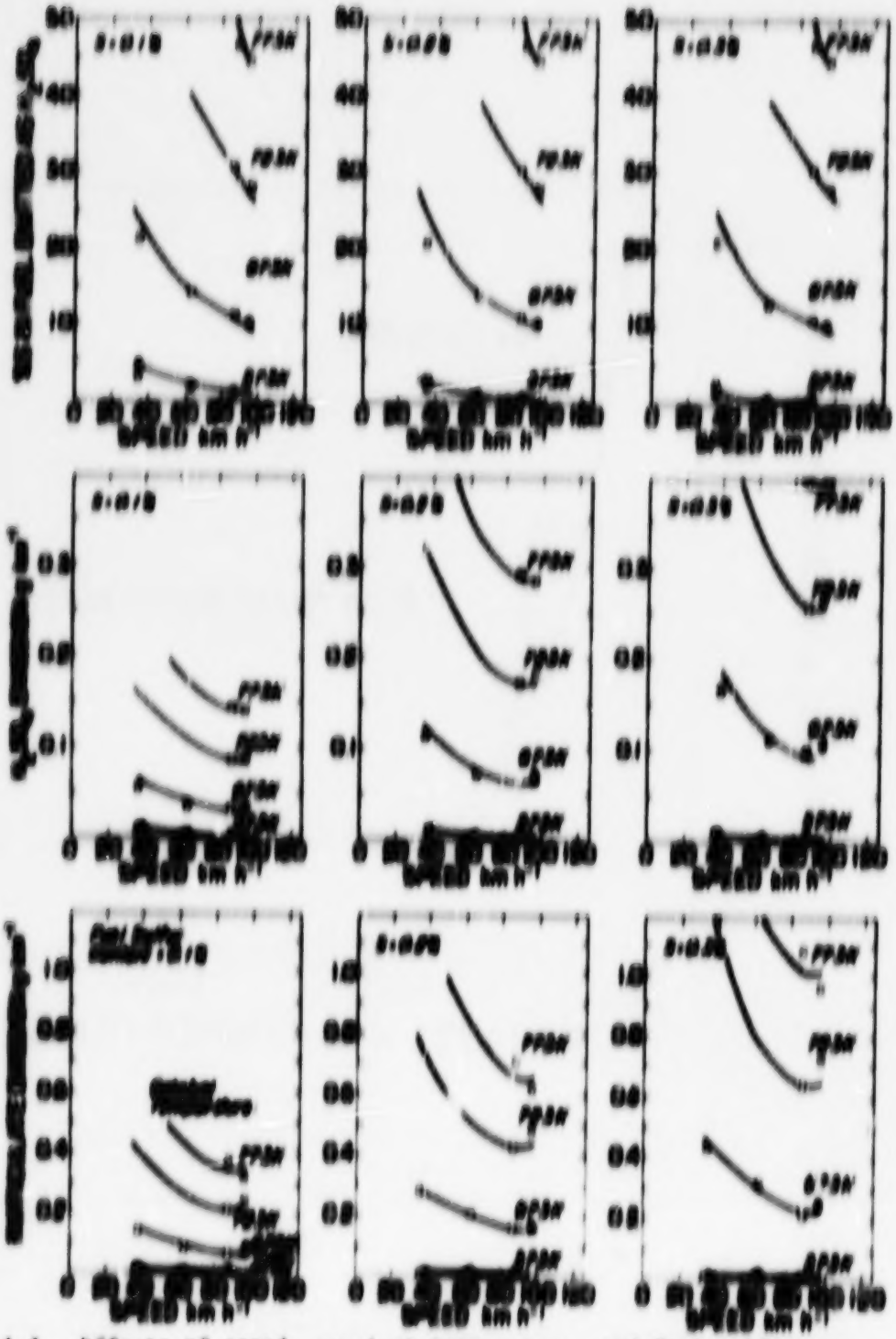


Fig. 4.5. Effects of speed, catalyst temperature, and fuel sulfur content on sulfur conversion, hydrocarbon emission and particulate emission. Indolene (0.0 fuel), A/F = 14.8, excess air = 25% (λ = 1.1). ○ piloted catalyst data ● monolithic catalyst data. Solid lines were calculated.

$$\text{Particulate emission} = A\left(\frac{C}{100}\right)F\left(\frac{S}{100}\right)(3.86) \quad g\ km^{-1} \qquad (4.1)$$

where A is a constant which is obtained by matching eq. (4.1) to the data. The data give A in the 2.2-2.8 range. The lines in Fig. 4.3 were computed using the average value of A=2.4. C is the percent conversion of SO_2 into SO_3 (see top of Fig. 4.3), F is the fuel consumption in g km^{-1} (Fig. 4.4) and S is the fuel sulfur content (percent sulfur per weight in the fuel).

Particulate emission under cyclic operation (7 mode Federal Test Procedure) are shown in Figs. 4.5 and 4.6. In these figures the ranges of particulate emissions at the steady speed corresponding to the average speed of the cycle (35 km h^{-1}) are also shown. For the 7 mode Federal Test Procedure the amount of particulate matter emitted increased linearly with the fuel sulfur content. A similar increase in particulate matter with fuel sulfur content was observed with the pelleted catalyst. With the monolithic catalyst at the steady 35 km h^{-1} speed the particulate emission seems to be insensitive to the fuel sulfur content. This can be explained by noting that the rate of reaction at which the SO_2 to SO_3 conversion occurs depends on the concentration of SO_2 in the exhaust gas at the inlet to the catalyst and on the catalyst temperature [20]. At low SO_2 concentrations and at high temperatures the mechanism limiting the formation of SO_3 is the adsorption of SO_2 by the catalyst. Under these conditions the reaction rate varies nearly linearly with the SO_2 concentration. At high SO_2 concentrations or low temperatures the rate of reaction becomes constant. In this region the reaction is controlled by desorption of SO_3 from the catalyst. In between the adsorption and desorption controlled regions the reaction is governed mostly by chemical reaction. The amount of particulate matter emitted is proportional

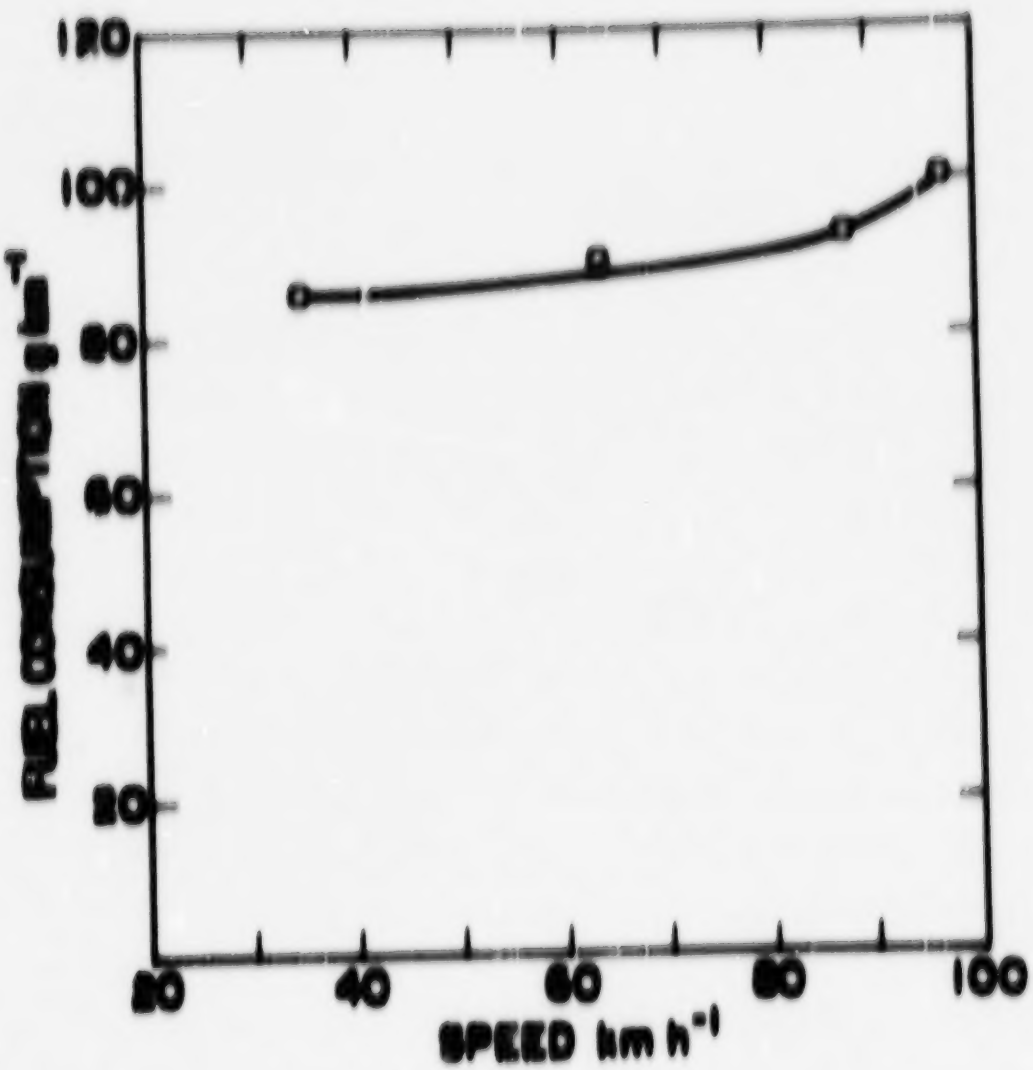
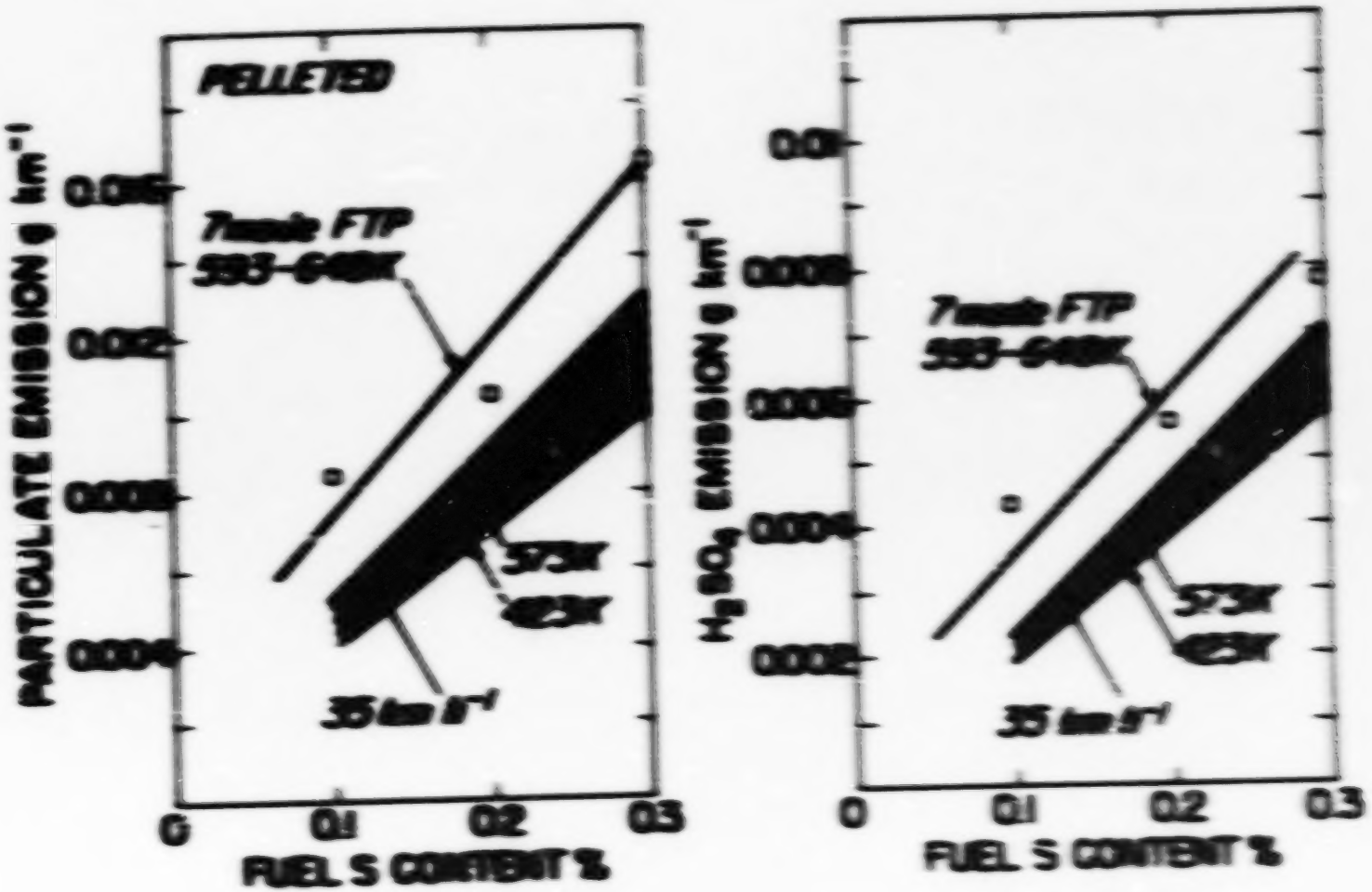


Fig. 1.1. Fuel consumption versus speed (...) for the data.


PELLETED
7 mode FTP
353-648K
573K
423K
35 km h⁻¹
PARTICULATE EMISSION g km⁻¹
0.006
0.002
0.0008
0.0004
0
0.1
0.2
0.3
FUEL S CONTENT %
H_2SO_4 EMISSION g km⁻¹
0.0008
0.0006
0.0004
0.0002
7 mode FTP
353-648K
573K
423K
35 km h⁻¹
0
0.1
0.2
0.3
FUEL S CONTENT %

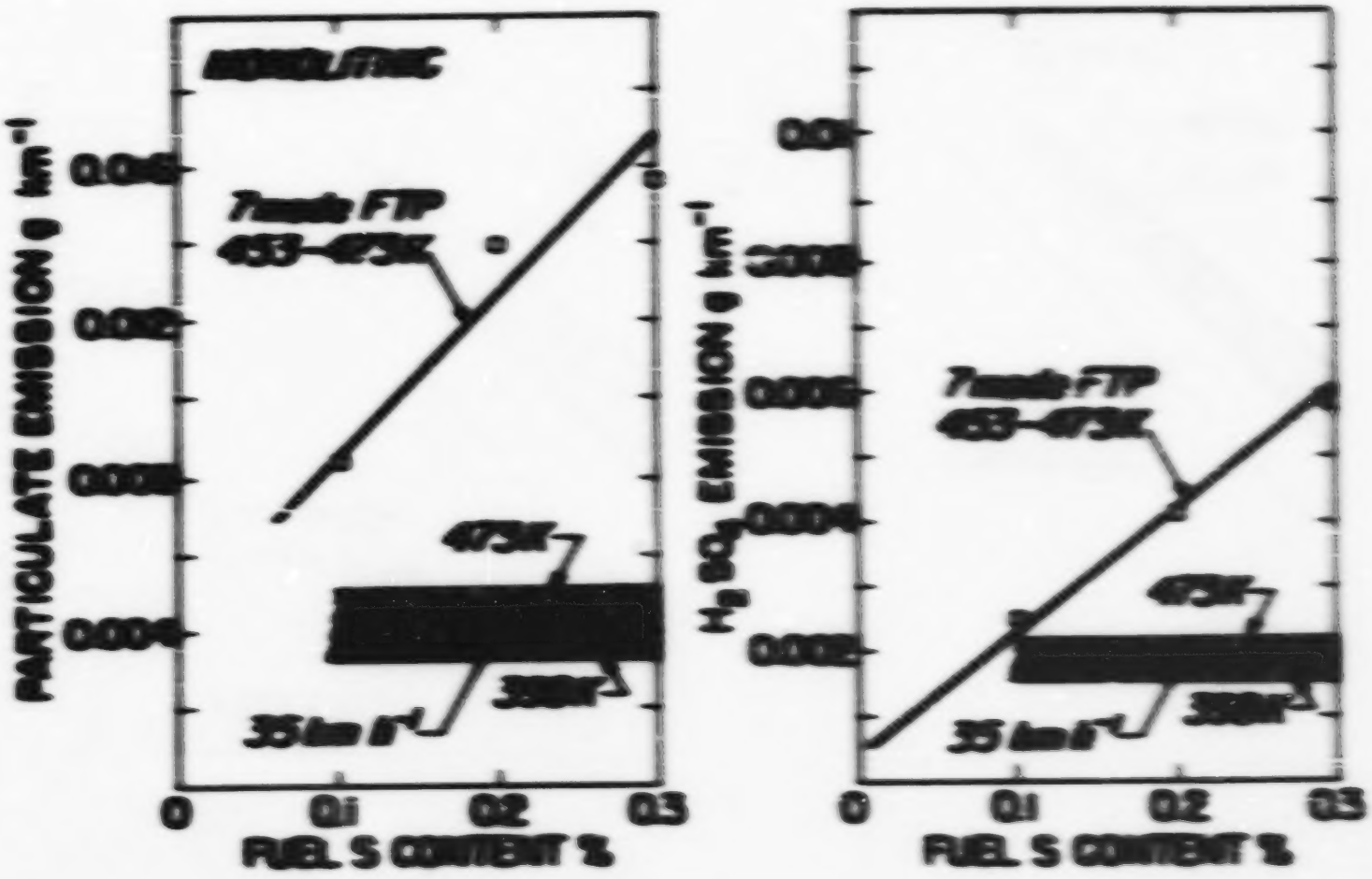


Fig. 5.4. [illegible] emission data: [illegible] fuel; [illegible] at 35 km h⁻¹ cruise [illegible]. [illegible] engine lubricant consumed in cruise operation [illegible] fuel.

to the sulfuric acid (i.e. SO_3 formed) in the exhaust (see next section). Thus, the fact that the amount of particulate matter emitted remained constant indicates that the reactions in the catalyst are in the desorption controlled region (high SO_2 concentration, low catalyst temperature) where the SO_2 concentration at the catalyst inlet does not affect the reaction. Since the amount of SO_2 is proportional to the fuel sulfur content, in this region the fuel sulfur content does not influence the results significantly. At higher catalyst temperatures the reactions are not in the desorption region and the amount of particulates emitted depends on the fuel sulfur content.

4.3 Sulfuric Acid Emission

The effects of speed, fuel sulfur content, and catalyst temperature on the amount of sulfuric acid emitted are shown in Fig. 4.5. There is a distinct similarity between the amounts of sulfuric acid and particulate matter emitted, because the particulates are composed mostly of sulfuric acid and water. The solid lines in Fig. 4.5 were calculated by the expression

$$\left(\frac{g_{H_2SO_4}}{km}\right)_{emission} = \left(\frac{S}{100}\right)\left(\frac{F}{100}\right)(9.06) \quad g\ km^{-1} \qquad (4.2)$$

The parameters S, F and 9 were defined in conjunction with eq. (4.1). Note that the sulfuric acid emission has a minimum at about 90 km h^{-1}. As will be shown in the next section the sulfur conversion decreases continuously with speed. However, the fuel consumption increases with speed (Fig. 4.4) giving rise to the minimum in the sulfuric acid emissions.

The sulfuric acid emission for the 7 mode Federal Test Procedure is shown in Fig. 4.5 and 4.6. As expected the trend in the results is the same as for the particulate emission because of the relationship between the amounts of sulfuric acid and particulate matter emitted.

4.5 Sulfur Conversion

The sulfur conversion (percent weight of sulfur in fuel converted to sulfuric acid) as a function of speed, fuel sulfur content, and catalyst temperature are shown in Fig. 4.6. The data points are from the measurements. The lines were computed according to the procedure described in Appendix D.

Note that for all the temperatures tested the sulfur conversion increases with temperature indicating that the catalytic reaction is kinetically limited (as opposed to being limited by chemical equilibrium) [20].

The results, cross-plotted using temperature as the abcissa and speed as the variable parameter, are shown in Fig. 4.7. The conversions were extrapolated to higher temperatures by calculating the reaction rate constants for higher temperatures using Arrhenius' equation (see Appendix D). The curves on the left side of the peaks correspond to reactions in the kinetically limited region, the ones on the right correspond to reactions in the region limited by chemical equilibrium. The data of Cornwick et al [3], Trayser et al [4], and Weir et al [7] obtained with a pelleted and monolithic catalyst are also included in Fig. 4.7. The data reported by these investigators were shifted 50 K to the right (as suggested by Dr. W.R. Pierson) to account for the fact that these investigators measured the catalyst temperature at the catalyst exit and not inside the catalyst.

Mikkor et al [8] also measured sulfur conversion. Their data are not included here because instead of an engine they used a simulated exhaust system. Nevertheless, their results show a trend similar to the curves in Fig. 4.7.

Figure 4.6 indicates that an increase in speed produces a decrease in sulfur conversion. The reason for this is that at higher speeds the flow rate through the catalyst increases decreasing the residence time inside the catalyst.

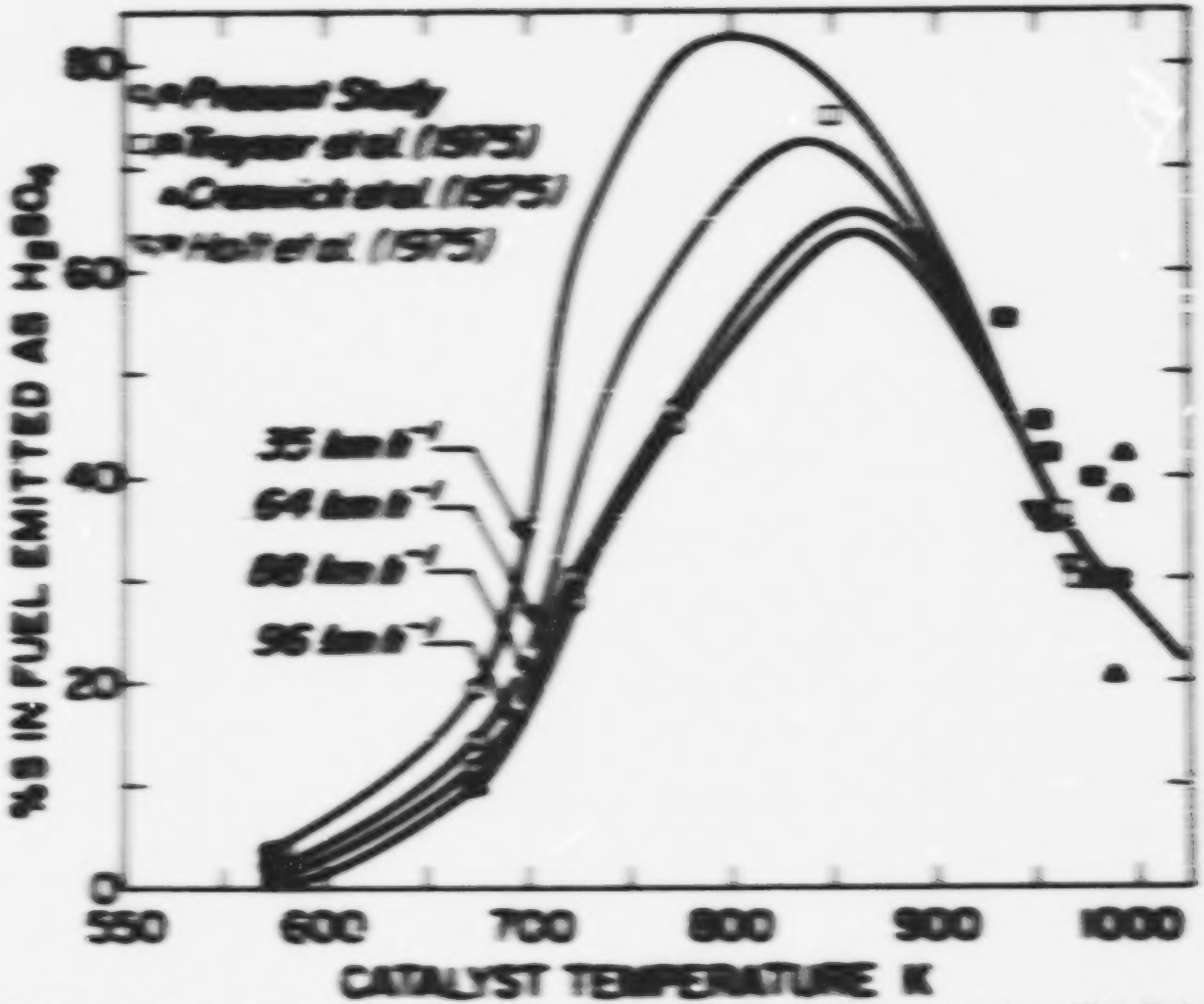

Present Study
Hofer et al. (1975)
%S IN FUEL EMITTED AS H_2SO_4
80
60
40
20
0
550
600
700
800
900
1000
CATALYST TEMPERATURE K

Fig. 4.7

Note that at catalyst temperatures above ≈ 900 K the reactions are in the chemical equilibrium region where the reactions are not affected by the flow rate, as observed by Ibiti et al [7].

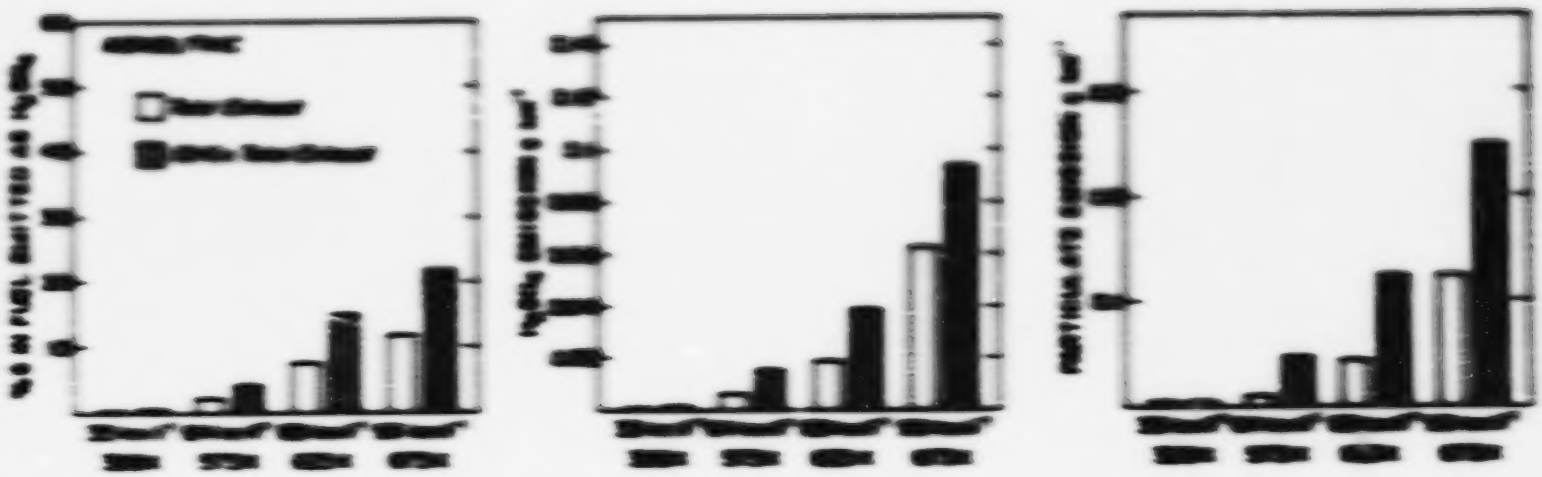
Figure 4.3 also shows the effect of fuel sulfur content on the sulfur conversion. The conversion is insensitive to the fuel sulfur content above ≈ 575 K indicating that the catalytic oxidation of SO_2 is limited by adsorption of SO_2 by the catalyst (see Section 4.1). Below ≈ 575 K the conversion decreases with fuel sulfur content indicating that the limiting mechanism is desorption of SO_3 from the catalyst.

4.4 Space Velocity

The effects of space velocity (i.e. the velocity of the exhaust gas through the catalyst) on particulate and sulfuric acid emissions and on the sulfur conversion are shown in Figs. 4.8 and 4.9. In general, a reduction in space velocity and a corresponding increase in residence time result in an increase of sulfuric acid conversion and hence an increase in the amounts of sulfuric acid and particulate matter emitted.

4.5 Secondary Air and Air Fuel Ratio

Sulfur conversion, sulfuric acid, and particulate emissions as a function of secondary air injected into the exhaust before the catalyst are given in Figs. 4.10 and 4.11. The amount of secondary air does not seem to affect the results suggesting that there is sufficient oxygen for the reaction to be completed. These results tend to agree with those reported by Nibbor et al [8]. At smaller amounts of secondary air, the secondary air might affect the results but the amounts needed to observe these effects could not be achieved in the present tests.



[illegible]

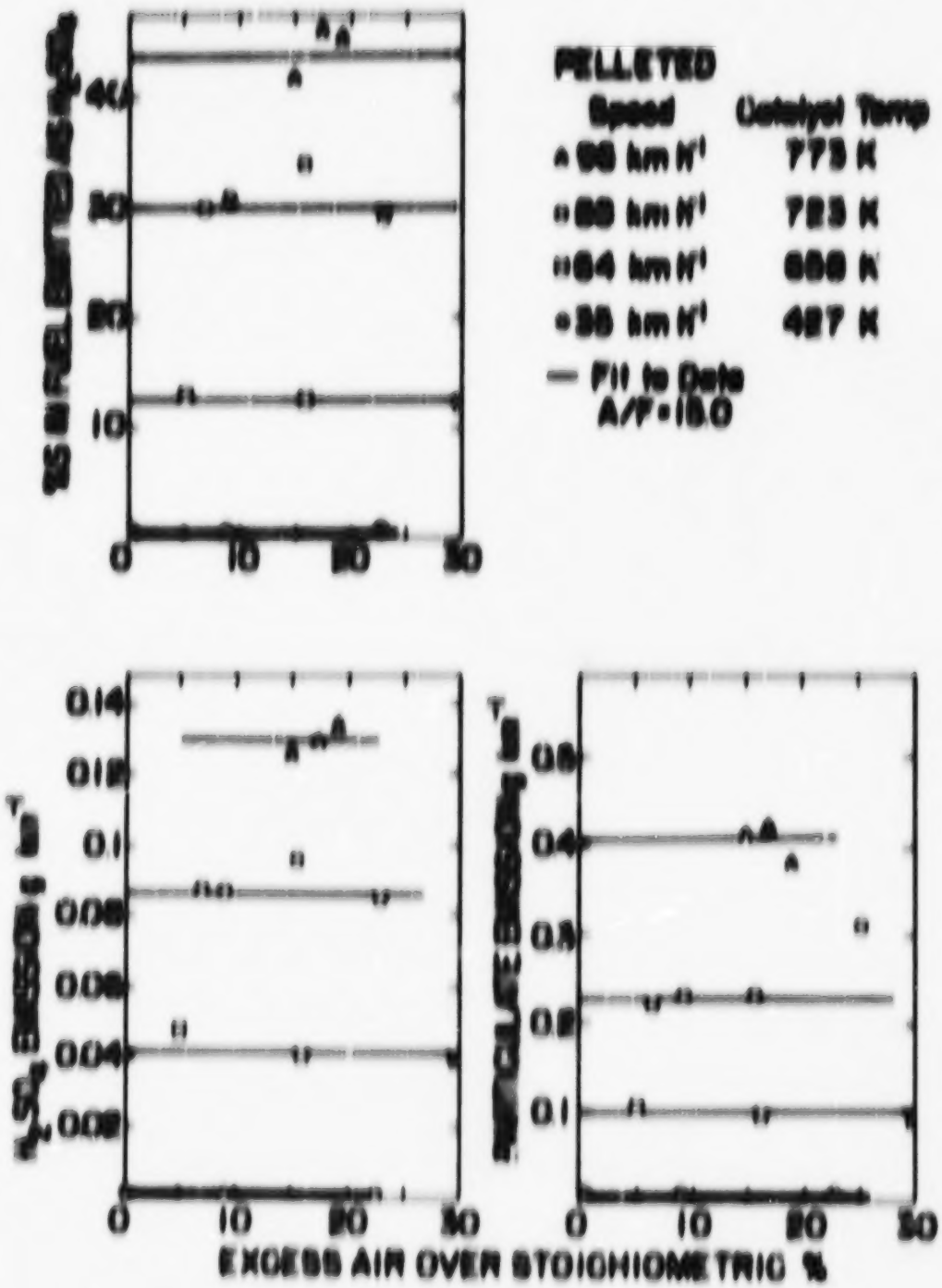


Fig. 4.10. Effect of secondary air on sulfur conversion, H_2S emission, and particulate emission for a pelleted catalyst. Indolene 80 fuel with 0.1% sulfur content.

% S IN FUEL EMITTED
AS H_2SO_4
H_2SO_4 EMISSION
g hr^{-1}

The air fuel ratio does not seem to influence the results provided the catalyst temperature is kept constant, and sufficient oxygen is supplied (through secondary air injection) to the catalyst to oxidise the unburned hydrocarbons, carbon monoxide, and sulfur dioxide (Fig. 4.12).

4.6 Concluding Remarks

The foregoing results indicate that the particulate emission, sulfuric acid emission, and sulfur conversion are nearly the same for both the monolithic and the pelleted catalyst provided the speed, the fuel sulfur content, and the catalyst temperature are the same for both catalysts. This implies that the emission is governed mostly by the operating parameters and depends less on the type of catalyst (pelleted or monolithic).

As noted before, in the present tests the operating conditions were set to indicate the effects of the various parameters individually on the emissions. In applying the results to actual operating conditions the appropriate combination of these parameters must be selected.

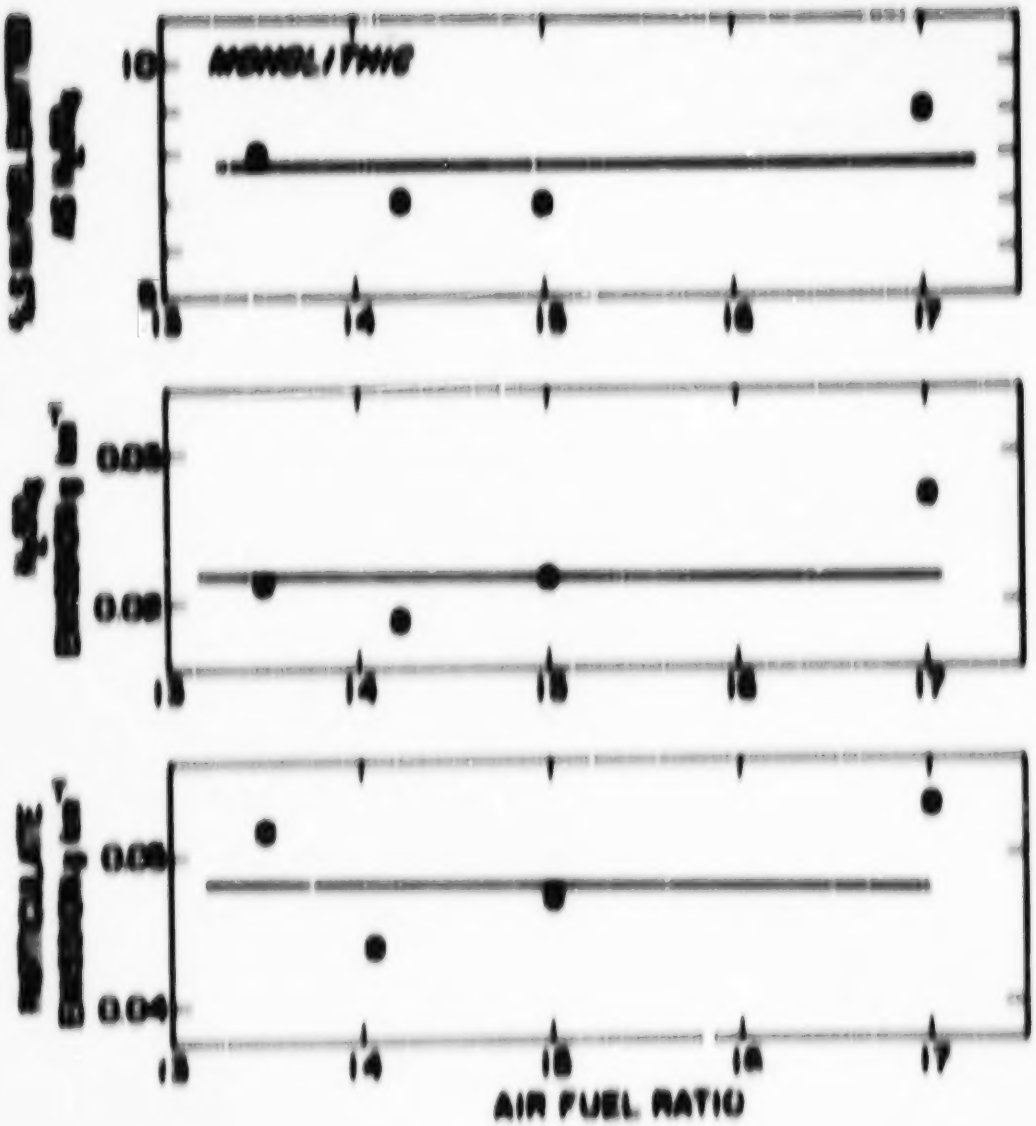


Fig. 4.12 Effect of air fuel ratio on sulfur conversion, H_2S emission, and particulate emission for a monolithic catalyst at the cruise condition. Excess air 25% (at 5% O_2) catalyst temperature 675 K. Indolene 30 fuel with 0.1% sulfur content (——) fit to data.

APPENDIX A

ENGINE SPECIFICATIONS AND OPERATING CONDITIONS

A.1 Engine Specifications

Displacement	350 cubic inches
Horsepower (adv.)	250 at 4800 RPM
Carburetor	2 barrel Rochester
Compression ratio	8.8:1
Bore	4.00 inches
Stroke	3.48 inches
Spark plugs	AC R45S
Point dwell	30 degrees

A.2 Steady Speeds

All tests at steady speeds were performed at conditions corresponding to a full sized 1970 Chevrolet cruising under road load conditions. The engine speed was calculated from

$$N = \frac{S' R}{\pi r} \qquad (A.1)$$

where S' is the car speed, R is the rear axle ratio, and r is the radius of the rear tires. For a standard Chevrolet R is 3.07 and r is 351 mm [21]. The load on the engine was calculated from

$$BHP = \frac{V}{550}\left(0.0021\,W + 0.0025\,A\,V^2\right) \qquad (A.2)$$

where V is the vehicle speed (km h^{-1}), W is the total weight of the car (17796.8 N) and A is the projected area of the automobile (2.88 m^2) [21].

A.3 Cyclic Operating Conditions

The cycle under which the engine was run was an approximation to the 7 mode Federal Test Procedure, Table A.1 [23, 25]. The cycle used in the tests is given in Table A.2.

A.4 Catalysts Specifications

Pelleted Catalyst:

The pelleted catalyst was a General Motors extrudate catalyst with a 5 to 1 platinum-palladium ratio and a nominal loading of 0.142 troy oz/cu ft.

Monolithic Catalyst:

The monolithic catalyst was an Engelhard PTX, type IIB catalyst.

Table A.1 Actual 7 Mode Federal Test Procedure

(The load is to be kept constant at 14 HP)

Mode	Speed km h^{-1}	Time, s	Cumulative time, s
	0 (idling)	20	20
I	0-48	14	34
II	48-48	15	49
III	48-24	11	60
IV	24-24	15	75
V	24-80	29	104
VI	80-15	25	129
VII	15-0 (idling)	8	137

Table A.2 Approximation to the 7 Mode Federal Test Procedure

(For every new mode the torque was set to the value necessary to produce 14 HP at the maximum rpm).

Mode	RPM	Time, s	Cumulative time, s
	700 (idling)	20	20
I	700-1150	14	34
II	1150-1150	15	49
III	1150-900	11	60
IV	900-900	15	75
V	900-1800	29	104
VI	1800.....	25	129
VII	700	8	137

APPENDIX B

PHYSICAL AND CHEMICAL PROPERTIES OF ISOOCTANE IFO 0

FUEL SUPPLIED BY AMOCO OIL COMPANY

Test	ASTM Method	Specification Control Limit	Test Values
API Gravity	D287	58.0-61.0	59.6-61.0
Distillation °F	D86		
Initial Boiling Point	D86	75-95	86-93
10% Evap.	D86	120-135	130-135
50% Evap.	D86	200-230	220-221
90% Evap.	D86	300-325	315-318
Maximum	D86	NMT 415	398-406
10% Slope	D86	NMT 5.2	2.9-5.9
Reid Vapor Pressure	D323	8.7-9.2	8.9-9.0
Oxidation Stability Minutes	D525	MIN 600	600+
Gum, mg/100 ml (after Heptane wash)	D381	NMT 4.0	0.2-3.0
TMEL grm. lead/gal.	D526	NMT 0.05	0.0-0.01
Sulfur Weight, %	D1266	NMT 0.10	0.01-0.017
Olefin, %	D1319	NMT 10	5.0-7.4
Aromatic, %	D1319	NMT 35	26.1-29.5
Saturates, %	D1319	Remainder	63.1-71.1
Octane Research (Clear)	D2699	95.0-98.5	96.5-97.4
Octane Research (3cc TEL/gal)	D2699	MIN 103.0	105.0-106.2
Phosphorus, gms./gal.	D3231	NMT 0.005	0.000-0.003
Sensitivity (Clear)		7.0-10.5	8.3-9.4
Sensitivity (3cc TEL/gal)		MIN 9.0	7.1-8.5

APPENDIX C

ENGINE AIR FLOW RATE AND FUEL FLOW RATE

C.1 Air Flow Rate

The air flow rate was measured during each test using a rounded approach air cart manufactured by General Motors Corporation. The pressure drop across the orifice was measured with a micromanometer and was related to the air flow rate by the expression

$$\dot{m}_{air} = K \sqrt{\Delta p \left(\frac{1}{R_{air}}\right)\left(\frac{p_{at}}{T_{air}}\right)} \qquad (C.1)$$

where K is a constant, Δp is the pressure drop across the nozzle (inches of water), T_{air} is the room temperature (deg R) and p_{at} is the atmospheric pressure (in Hg).

C.2 Fuel Flow Rate

The fuel volume flow rate was measured with a burette. In calculating the mass flow rate the fuel density was taken to be 0.74 g cm^{-3}.

APPENDIX D

CALCULATION OF THE CONVERSION OF SO_2 TO SO_3

SO_3 is produced by the reaction

$$SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons SO_3 \qquad (D.1)$$

In order to calculate the rate constant k it is assumed that the above reaction is a first order, reversible reaction. For such a reaction the rate constant (dm^3/(hr·catalyst mass in kg)) is given by [20]

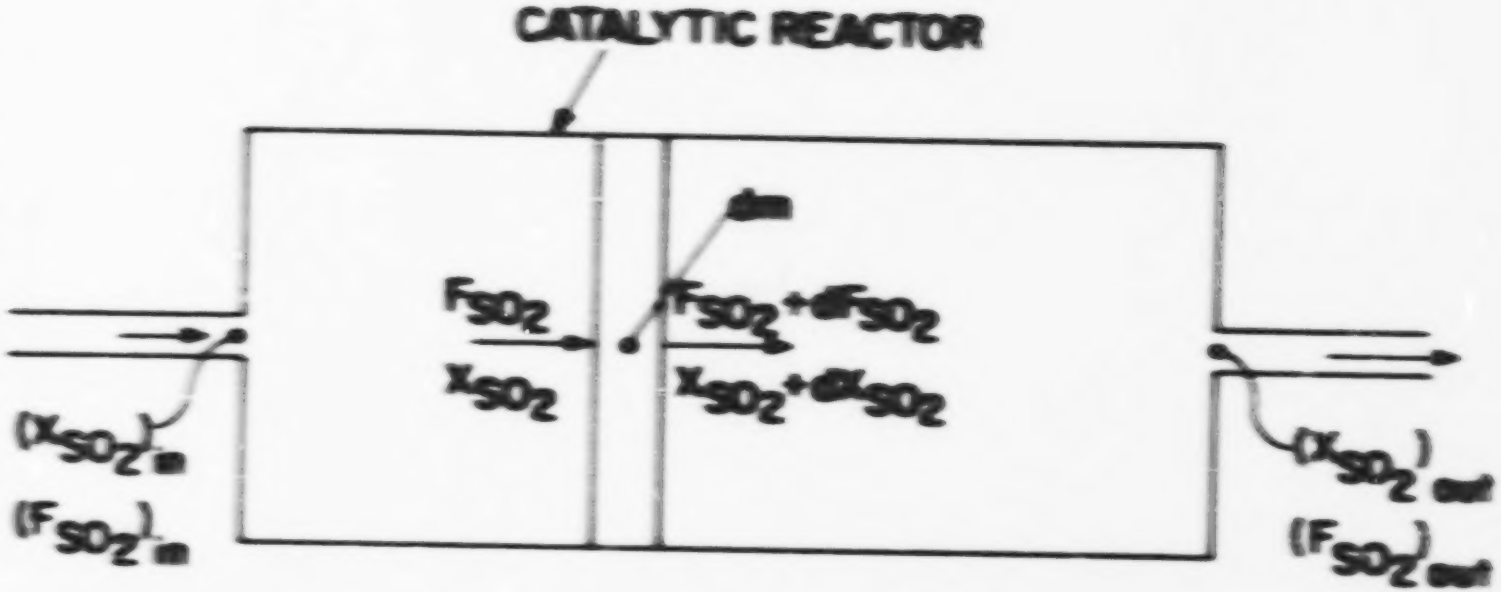
$$k = \frac{-r_{SO_2}}{C_{SO_2} - (C_{SO_2})_e} \qquad (D.2)$$

where $(-r_{SO_2})$ is the rate of disappearance of SO_2 (moles of SO_2 reacted/catalyst mass kg · h), C_{SO_2} is the concentration of SO_2 (moles/dm^3) at a given position inside the catalyst, $(C_{SO_2})_e$ is the chemical equilibrium concentration of SO_2 (moles/dm^3). r_{SO_2} and C_{SO_2} are not known directly but must be determined from the information available which are the amount of SO_2 entering the catalyst (reactor) and the amount of SO_3 leaving the catalyst. In order to utilize the available information we assume that the reaction takes place in a plug flow type reactor shown in Fig. D.1. For a differential element containing a dm mass of the catalyst an SO_2 mass balance gives [20]

$$(F_{SO_2})_{in}\, d\,x_{SO_2} = -r_{SO_2}\, dm \qquad (D.3)$$

Upon integration eq. (D.3) becomes

$$\frac{m}{(F_{SO_2})_{in}} = \int_{(F_{SO_2})_{in}}^{(F_{SO_2})_{out}} \frac{d\,x_{SO_2}}{r_{SO_2}} \qquad (D.4)$$


CATALYTIC REACTOR
dm
F_{SO_2}
$F_{SO_2}+dF_{SO_2}$
X_{SO_2}
$X_{SO_2}+dX_{SO_2}$
$(X_{SO_2})_{in}$
$(F_{SO_2})_{in}$
$(X_{SO_2})_{out}$
$(F_{SO_2})_{out}$

m is the mass of the catalyst in the reactor, (F_{SO_2}) is the molar flow of SO_2, (x_{SO_2}) is the fraction of SO_2 converted into SO_3. The subscripts in and out represent the conditions at the inlet and outlet of the reactor, respectively.

$$(x_{SO_2})_{out} = \frac{(c_{SO_3})_{out}}{(c_{SO_2})_{out} + (c_{SO_3})_{out}} \tag{D.5}$$

By assuming that $(x_{SO_2})_{in} = 0$, and substituting eq. (D.2) into (D.4) we obtain

$$\frac{m}{(F_{SO_2})_{in}} = \int_0^{(x_{SO_2})_{out}} \frac{dx_{SO_2}}{k\left(c_{SO_2} - (c_{SO_3})_\beta\right)} \tag{D.6}$$

With the definitions

$$x_{SO_2} = \frac{c_{SO_3}}{c_{SO_2} + c_{SO_3}} = \frac{(c_{SO_2})_{in} - c_{SO_2}}{(c_{SO_2})_{in}} \tag{D.7a}$$

$$(x_{SO_2})_\beta = \frac{(c_{SO_3})_\beta}{(c_{SO_2})_\beta + (c_{SO_3})_\beta} = \frac{(c_{SO_2})_{in} - (c_{SO_2})_\beta}{(c_{SO_2})_{in}} \tag{D.7b}$$

eq. (D.6) yields

$$k\,\frac{m}{(F_{SO_2})_{in}}\,(c_{SO_2})_{in} = \int_0^{(x_{SO_2})_{out}} \frac{dx_{SO_2}}{(x_{SO_2})_\beta - x_{SO_2}} \tag{D.8}$$

The subscript β denotes chemical equilibrium. Integration of eq. (D.8) gives

$$k = \frac{\ln \dfrac{(x_{SO_2})_\beta}{(x_{SO_2})_\beta - (x_{SO_2})_{out}}}{m\,\dfrac{(c_{SO_2})_{in}}{(F_{SO_2})_{in}}} \tag{D.9}$$

The following calculations were performed for $\alpha = 1$ i.e. $(x_{SO_2})_\beta$ as a function of temperature was obtained by Hamberte et al [3]. Their result is reproduced here in fig. D.1. $(x_{SO_2})_{out}$ was measured in

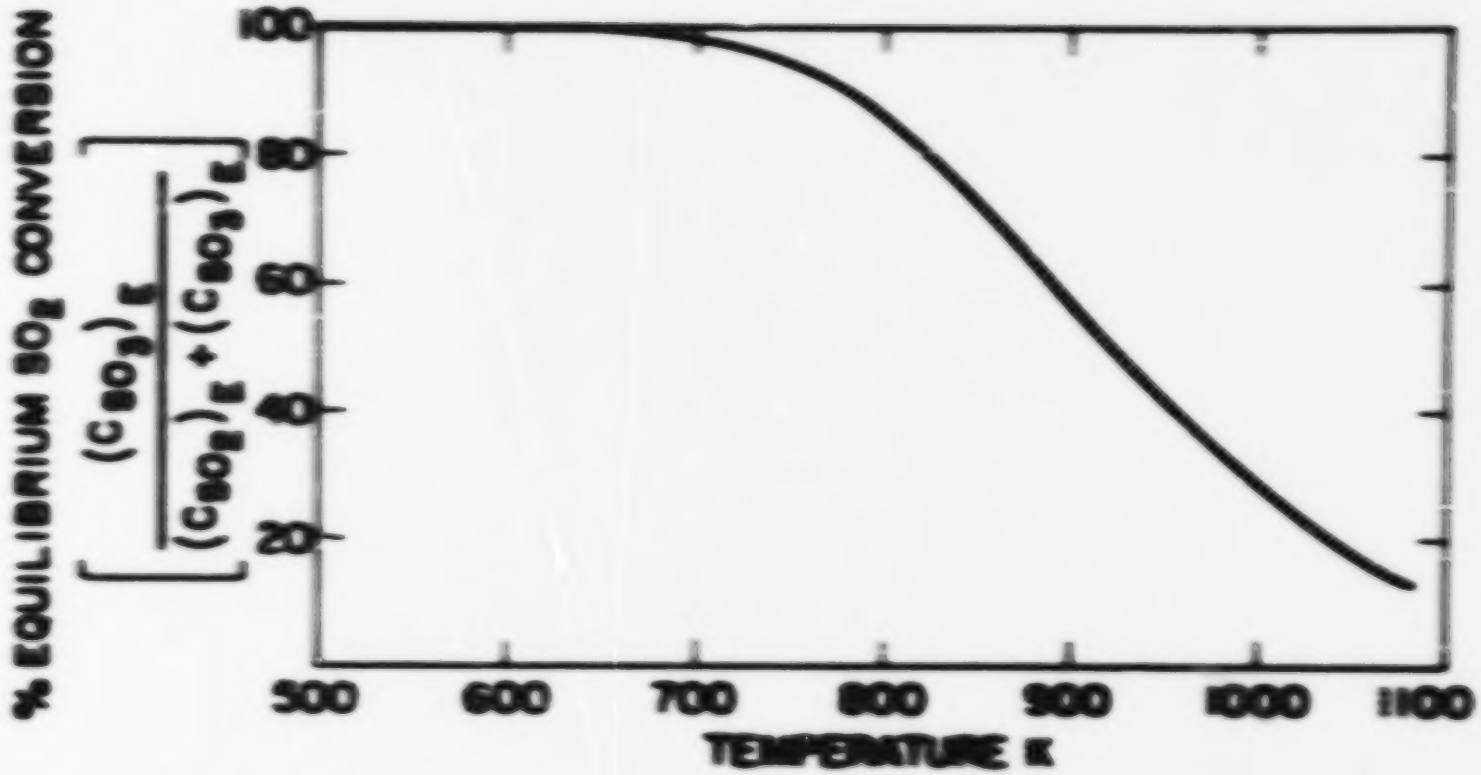


Fig. 1.1 Conversion of SO_2 to SO_3 at chemical equilibrium (from Hamrick and Walker [9])

the present experiments. The results of the measurements are shown in the top three plots of Fig. 4.5. Note that % conversion is the same as $100 \times (\%SO_2)_{out}$.

$(\%SO_2)_{in}$ was determined as follows. The catalyst was operated with 25 percent excess over stoichiometric. This corresponds to an "air fuel ratio" of 18:1 through the catalyst. The "air fuel ratio" through the catalyst is defined as

$$(A/F)_{cat} = \frac{\text{mass of air flowing through catalyst}}{\text{mass of fuel burned in the engine}} = \frac{m_a}{m_f} \quad (D.10)$$

The amount of sulfur per kg of exhaust gas is

$$m_S = \frac{m_f}{m_a + m_f} \cdot \frac{S}{100} \quad (D.11)$$

where S is the percent sulfur in the fuel by weight. The number of moles of SO_2 per kg of exhaust gas is

$$(C_{SO_2}) = \frac{m_S}{32} \quad \frac{\text{kg mole}}{\text{kg exhaust}} \quad (D.12)$$

since one mole of S in the fuel gives rise to one mole of SO_2.

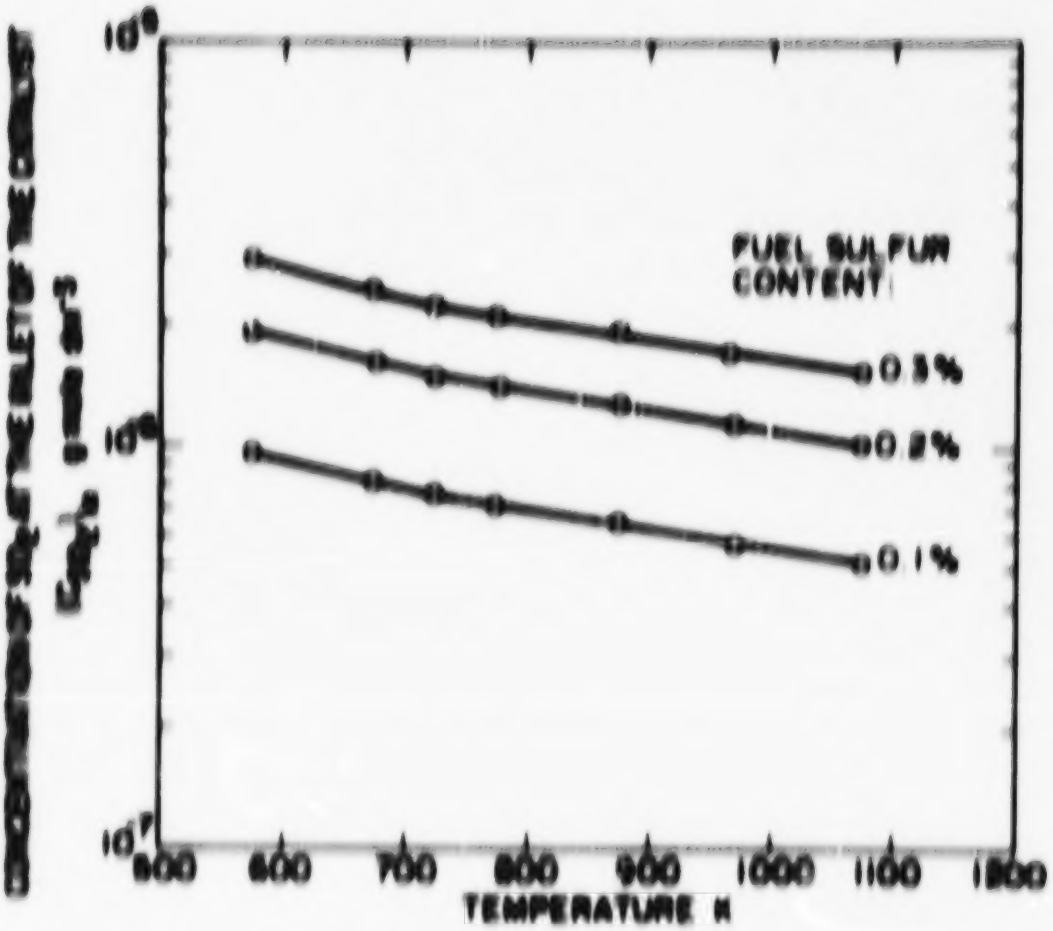
Equations (D.10), (D.11) and (D.12) give

$$(C_{SO_2})_{in} = \frac{1000}{(A/F)(32)(100)} \cdot S \quad \frac{\text{g mole}}{\text{kg exhaust}} \quad (D.13)$$

or

$$(C_{SO_2})_{in} = \frac{1000}{(A/F)(32)(100)} \cdot S \cdot \rho_{exh} \quad \frac{\text{g mole}}{\text{cm}^3 \text{ exhaust}} \quad (D.14)$$

where ρ_{exh} is the density of the exhaust gas. This density was calculated by assuming that the density of the exhaust gas is the same as the density of air at the temperature and pressure of the exhaust. The results are shown in Fig. D.1.


FUEL SULFUR CONTENT
0.5%
0.2%
0.1%
TEMPERATURE K

In eq. (D.9) $(F_{SO_2})_{in}$ is the number of moles of SO_2 entering the catalyst per hour

$$(F_{SO_2})_{in} = \frac{\text{g fuel burned}}{\text{hour}} \left(\frac{S}{100}\right)\left(\frac{1}{32}\right) \quad \frac{\text{moles}}{\text{hour}} \tag{D.15}$$

The results for $(F_{SO_2})_{in}$ are given in Table D.1.

In order to obtain k, eq. (D.9) was plotted in Fig. D.4 for various temperatures. The slope of the lines gives the rate constant. The rate constant as a function of inverse temperature is represented in Fig. D.5.

Arrhenius' equation gives the rate constant as [20]

$$k = A e^{-\frac{E}{RT}} \tag{D.16}$$

where A and E are two constants, R is the ideal gas constant (R = 8.28 joule/gmol K) and T is the absolute temperature (degrees K). From the line in Fig. D.5 the values for A and E are E = 87,450 joule/gmol K, A = 3.3 x 10^{11}. By knowing k the sulfur conversion can be readily calculated from eq. (D.9), i.e.

$$(X_{SO_2})_{out} = (X_{SO_2})_E \left(1 - e^{-\frac{k\, m_{Pt}}{(F_{SO_2})_{in}}}\right) \tag{D.17}$$

Table 8.1 Molar flow of NO_x into the catalyst

Speed km h^{-1}	Fuel consumption kg h^{-1}	$(FNO_x)_{in}$ g moles h^{-1}
96	10.0	0.32
88	8.4	0.26
64	5.8	0.19
32	5.0	0.08

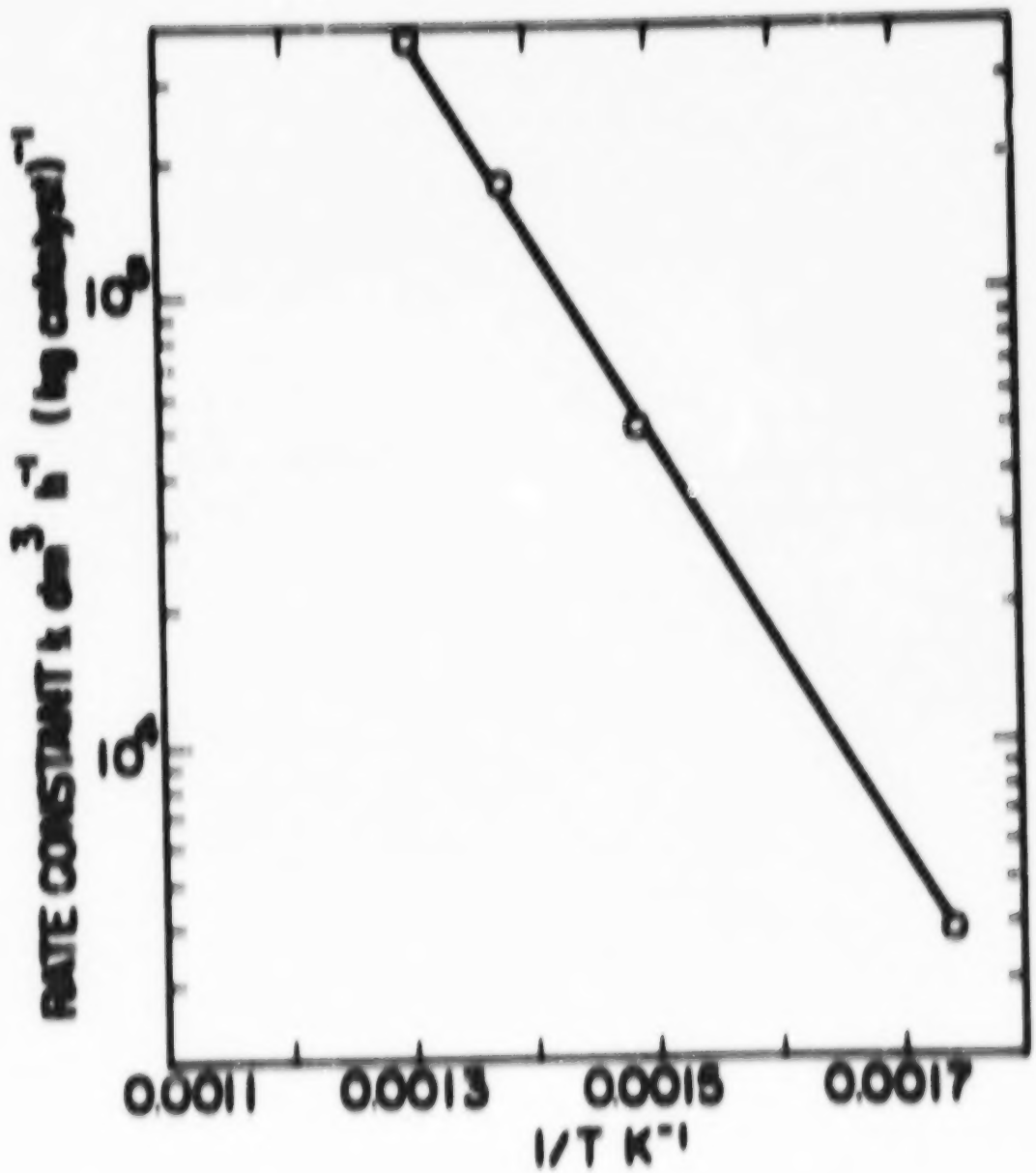


Fig. 6.5 Rate constant as a function of temperature for the reaction [illegible]

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